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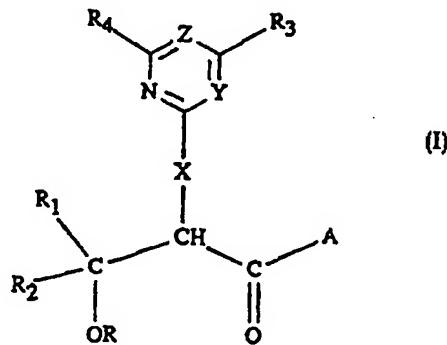
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(54) Title: PYRIMIDINYL- AND TRIAZINYL-OXY AND THIO-3-HALOALKYL-PROPIONIC ACID DERIVATIVES AS HERBICIDES

(57) Abstract

Compounds of formula (I), wherein R_1 is C_1-C_7 haloalkyl; X is oxygen or sulfur; and salts of compounds of formula (I) that contain a carboxy or sulfonamide group, and stereoisomers of the compounds of formula (I), are suitable as active ingredients in compositions for controlling weeds.



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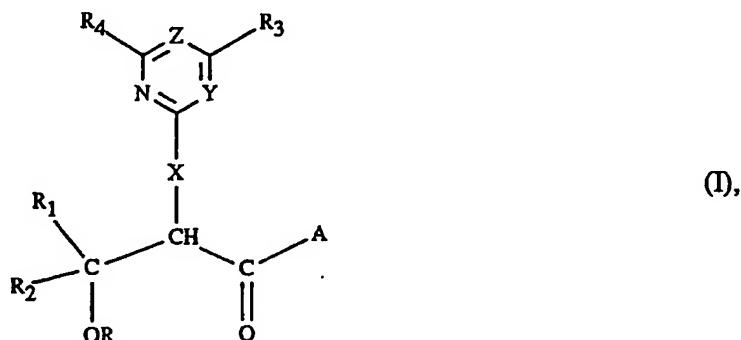
PYRIMIDINYL- AND TRIAZINYL-OXY AND THIO-3-HALOALKYL-PROPIONIC ACID DERIVATIVES AS HERBICIDES

The present invention relates to novel herbicidally active pyrimidinyl- and triazinyl-oxy- and -thio-3-haloalkyl-propionic acid derivatives, to processes for the preparation thereof, to compositions comprising those compounds and to the use thereof in the control of weeds, especially in crops of useful plants or in the inhibition of plant growth.

2- and 4-pyrimidinyl- and triazinyl-oxy- and -thio-propionic acid derivatives having herbicidal activity are known and are described, for example, in EP-A-0 347 811, EP-A-0 400 741, EP-B-0 409 368, EP-B-0 411 706, EP-A-0 481 512, EP-A-0 517 215, EP-A-0 541 041, EP-A-0 549 079, EP-A-0 567 014, EP-A-0 562 510, EP-A-0 581 184, DE-A-3 807 532, WO 93/25540 and WO 94/25442.

Novel pyrimidinyl- and triazinyl-oxy- and -thio-3-haloalkyl-propionic acid derivatives having herbicidal and growth-inhibiting properties have now been found.

The present invention therefore relates to compounds of formula I



wherein

- R is hydrogen, C₁-C₆alkyl, C₁-C₄haloalkyl, C₁- or C₂-alkyl substituted by C₁- or C₂-alkoxy, cyano, phenyl or phenyl substituted by halogen, methyl, methoxy or trifluoromethyl, C₃-C₆alkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl-C₁- or -C₂-alkyl, C₄-C₆cycloalkyl, C₁-C₄alkylcarbonyl or C₁-C₄alkylsulfonyl;
- R₁ is C₁-C₇haloalkyl;
- R₂ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₂-C₆alkenyl, C₃-C₆cycloalkyl, phenyl, phenyl substituted by fluorine, chlorine, bromine, trifluoromethyl or methoxy, 2-, 3-

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or 4-pyridyl, or 2- or 3-thienyl;

R₃ is methyl, ethyl, methoxy, ethoxy, trifluoromethyl, difluoromethoxy or 2,2,2-trifluoroethoxy;

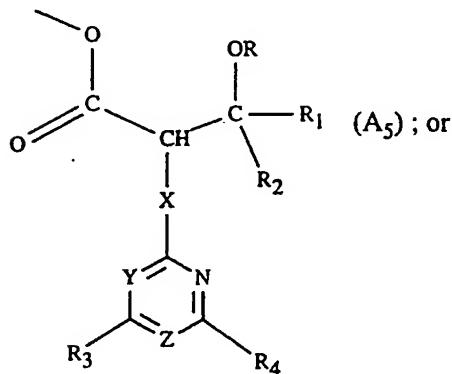
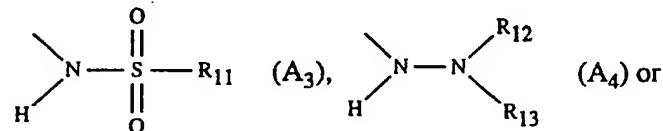
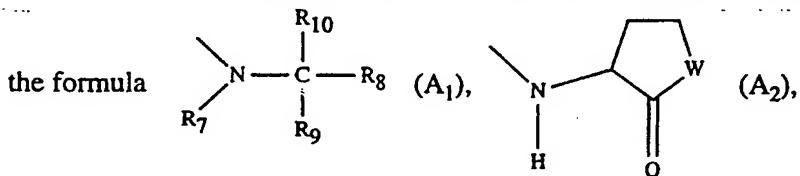
Z is nitrogen, methine or methine substituted by fluorine, chlorine, bromine or methyl;

R₄ is fluorine, chlorine, methyl, ethyl, isopropyl, cyclopropyl, methoxy, ethoxy, methylthio, ethylthio, methylamino, dimethylamino, ethylamino, methoxymethyl, trifluoromethyl, chloromethyl, trichloromethyl or difluoromethoxy; or, if Z is methine, R₄ forms a -O(CH₂)_m- bridge to Z, the linkage to Z being *via* the carbon atom;

Y is nitrogen, or, if Z is nitrogen, Y is nitrogen, methine or methine substituted by fluorine, chlorine or bromine;

X is oxygen or sulfur;

A is hydroxy, -OR₅, -SR₆, imidazolyl, triazolyl, 2-thionothiazolidin-3-yl, cyanamino, hydroxyamino, C₁-C₆alkoxyamino, C₁-C₃alkoxy(C₁-C₃alkyl)amino or a group of



A and R together form a bond;

R₅ is C₁-C₆alkyl, C₃-C₆alkenyl, C₃-C₆alkynyl, C₁-C₄alkoxy-C₁-C₄alkyl, C₁- or C₂-alkoxy-ethoxy-C₁- or -C₂-alkyl, C₃- or C₄-alkenyl-alkoxy-C₁-C₄alkyl, C₃- or C₄-alkynyl-alkoxy-C₁-C₄alkyl, C₁-C₄alkylthio-C₁-C₄alkyl, C₁-C₄alkylsulfinyl-C₁-C₄alkyl, C₂-C₄dialkylamino-C₁-C₄alkyl, tri-C₁-C₆alkyl-silyl-C₁-C₄alkyl,

C_1 - C_4 alkylcarbonyloxy- C_1 - or - C_2 -alkyl, C_1 - C_4 alkoxycarbonyl- C_1 - C_6 alkyl, C_3 - or C_4 -alkenyloxy carbonyl- C_1 - C_6 alkyl, C_3 - or C_4 -alkynyloxy carbonyl- C_1 - C_6 alkyl, C_1 - C_4 alkylthiocarbonyl- C_1 - C_4 alkyl, benzyloxycarbonyl- C_1 - C_6 alkyl, C_1 - C_4 alkoxy-carbonylmethyl-carbonylmethyl, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkyl- C_1 - C_3 alkyl, C_3 - C_6 oxacycloalkyl, C_3 - C_6 oxacycloalkyl substituted by C_1 - C_3 alkyl, C_2 - C_6 oxacycloalkyl- C_1 - C_3 alkyl, C_3 - C_5 dioxacycloalkyl, C_3 - C_5 dioxacycloalkyl substituted by C_1 - C_3 alkyl, C_3 - C_5 dioxacycloalkyl- C_1 - C_3 alkyl, benzyl, pyridylmethyl, C_1 - or C_2 -di-alkyl-phosphinyl, C_1 - C_4 alkylamino, dimethylamino, C_2 - C_6 alkylideneimino, (C_2 - C_6 alkylideneimino)-oxy- C_1 - or - C_2 -alkyl, phenyl, or phenyl substituted by fluorine, chlorine, bromine, methyl, methoxy or nitro;

R_6 is C_1 - C_6 alkyl, C_2 - C_4 dialkylamino- C_1 - C_4 alkyl, C_1 - C_4 alkoxycarbonyl- C_1 - C_4 alkyl, phenyl, or phenyl substituted by fluorine, chlorine, bromine, methyl, methoxy or nitro;

R_7 is hydrogen or methyl;

R_9 is hydrogen, trifluoromethyl, C_1 - C_4 alkyl, C_1 - C_4 alkyl substituted by hydroxy, C_1 - C_4 alkoxy, mercapto, C_1 - C_4 alkylmercapto, phenyl, 4-hydroxyphenyl, 4-imidazolyl, 3-indolyl, carboxy, C_1 - C_4 alkoxycarbonyl, C_3 - or C_4 -alkenyloxy carbonyl, cyano, carbamoyl, methylphosphino or methylsulfoximino, C_2 - C_6 alkenyl, C_2 - C_6 alkenyl substituted by chlorine, methyl or methoxy, ethynyl, cyclopropyl, phenyl or phenyl substituted by chlorine, methyl or methoxy; or

R_7 and R_9 together are $-(CH_2)_q$ -, $-CH_2CH(OH)CH_2$ -, $-CH_2SCH_2$ - or $-CH_2CH_2SCH_2$;

R_8 is hydroxymethyl, formyl, cyano, phosphono, phosphino, methylphosphino or a -COL group;

R_{10} is hydrogen or methyl; or

R_9 and R_{10} together are $-(CH_2)_n$ -;

R_{11} is C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyl, C_2 - C_6 alkynyl, C_2 - C_6 haloalkynyl, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkylmethyl, C_1 - C_4 alkylamino, di- C_1 - C_4 alkylamino, C_1 - C_3 alkoxy- C_1 - C_3 alkylamino, C_3 - C_6 alkenylamino, C_3 - C_6 alkynylamino, C_3 - C_6 cycloalkylamino, morpholino, piperazino, piperidino, arylamino, arylamino substituted by fluorine, chlorine, methyl, trifluoromethyl, methoxy or benzylamino, pyridyl, pyridyl substituted by fluorine, chlorine, methyl, ethyl, methoxy, methylamino, C_1 - C_3 alkoxycarbonyl, difluoromethoxy or trifluoromethyl, benzyl, phenyl or phenyl substituted by fluorine, chlorine, bromine, methyl, ethyl, trifluoromethyl, methoxy, difluoromethoxy, ethoxy, nitro, cyano or C_1 - C_3 alkoxycarbonyl;

R_{12} is hydrogen or methyl;

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R_{13} is hydrogen, C_1 - C_6 alkyl, phenyl or phenyl substituted by fluorine, chlorine, bromine, iodine, C_1 - C_4 alkyl, trifluoromethyl, C_1 - C_3 alkoxy, difluoromethoxy, cyano, nitro or C_1 - C_4 alkoxycarbonyl, pyridyl or pyridyl mono- or di-substituted by fluorine, chlorine, methyl, methoxy or trifluoromethyl;

m is 2 or 3;

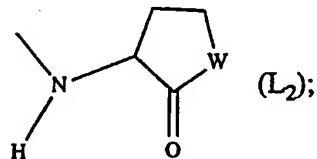
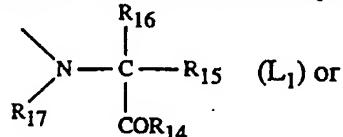
n is 2, 3, 4 or 5;

q is 2 or 3;

W is oxygen or sulfur;

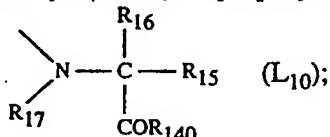
L is hydroxy, C_1 - C_4 alkoxy, C_3 - or C_4 -alkenyloxy, amino, C_1 - C_4 alkylamino, C_1 - C_4 di-

alkylamino, benzyloxy or a group of the formula



R_{14} is hydroxy, C_1 - C_4 alkoxy, 2-propenyloxy, benzyloxy, amino or a further group of the

formula



R_{140} is hydroxy, C_1 - C_4 alkoxy, 2-propenyloxy, benzyloxy or amino;

R_{15} is hydrogen, C_1 - C_4 alkyl or benzyl;

R_{17} is hydrogen; or

R_{15} and R_{17} together are $-(CH_2)_3-$; and

R_{16} is hydrogen or methyl;

and salts of compounds of formula I that contain a carboxy or sulfonamide group, and stereoisomers of the compounds of formula I.

The compounds of formula I contain at least one asymmetric carbon atom. That means that the compounds can occur in optically isomeric forms. If an aliphatic $C=C$ double bond is present, geometric isomerism (E or Z form) can also occur. That applies especially in the case of those compounds of formula I wherein the radicals R , R_2 , R_5 , R_9 and R_{11} are alkenyl. Formula I thus includes all the possible stereoisomers present in the form of enantiomers, diastereoisomers, E/Z isomers or mixtures thereof.

In formula I the alkyl radicals may be straight-chained or branched. The same applies also to the/each alkyl moiety of alkoxy, alkylthio, alkylsulfinyl, alkylsulfonyloxy, alkylamino, dialkylamino, alkylsilyl, alkoxycarbonyl, alkylcarbonyloxy, haloalkyl groups and other alkyl-containing groups.

In the definitions, C_1 - C_6 alkyl is, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl or the isomers of pentyl, and hexyl or the isomers of hexyl.

An alkoxy-, cyano- or phenyl-substituted alkyl group is, for example, methoxyethyl, ethoxyethyl, cyanoethyl or benzyl.

Alkoxyethoxy-substituted alkyl groups in the definition of R_5 are, for example, methoxyethoxymethyl.

The C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyl and C_3 - C_6 alkynyl radicals occurring in the substituents may likewise be straight-chained or branched, such as vinyl, allyl, methallyl, 1-methylvinyl, but-2-en-1-yl, 3-chloro-2-propenyl, 3-chloro-2-methyl-2-propenyl, 2,3-dichloro-2-propenyl, 2-propyn-1-yl, 1-methyl-2-propyn-1-yl and but-2-yn-1-yl.

Alkoxy is, for example, methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy or tert-butoxy.

Alkenyloxy is, for example, allyloxy, methallyloxy or but-2-en-1-yloxy.

Alkynyloxy is, for example, 2-propyn-1-yloxy, 2-butyn-1-yloxy or 3-butyn-1-yloxy.

Alkylamino is, for example, methylamino, ethylamino, n-propylamino, isopropylamino, n-butylamino or sec-butylamino.

Dialkylamino is, for example, dimethylamino or diethylamino.

Alkoxy(alkyl)amino is, for example, N-methoxy(methyl)amino.

Alkenylamino is, for example, 2-propenylamino.

Alkynylamino is, for example, 2-propynylamino.

Cycloalkylamino is, for example, cyclopropylamino.

Alkylthio or alkylmercapto is, for example, methylthio, ethylthio, n-propylthio, isopropylthio, n-butylthio, sec-butylthio or tert-butylthio.

Alkylideneimino is, for example, 2-propylideneimino or 2-butyldeneimino.

Alkoxy carbonyl is, for example, methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, isopropoxycarbonyl, n-butoxycarbonyl or tert-butoxycarbonyl.

A haloalkyl group may contain one or more halogen atoms, such as fluorine, chlorine or bromine, for example fluoromethyl, difluoromethyl, chloromethyl, dichloromethyl, dibromomethyl, 2-fluoroethyl, 2,2,2-trifluoroethyl, 2-chloroethyl or 2,2,2-trichloroethyl. There may be mentioned as examples of a polyhalogenated alkyl group trifluoromethyl, chlorodifluoromethyl, dichlorofluoromethyl, trichloromethyl, tribromomethyl, pentafluoroethyl and heptafluoropropyl.

Cycloalkyl radicals that are suitable as substituents are, for example, cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

Cycloalkyl-C₁-C₃alkyl radicals that are suitable as substituents are, for example, cyclopropyl-methyl, cyclopropyl-ethyl, cyclopropyl-propyl, cyclobutyl-methyl, cyclobutyl-ethyl, cyclobutyl-propyl, cyclopentyl-methyl, cyclopentyl-ethyl, cyclopentyl-propyl, cyclohexyl-methyl and cyclohexyl-ethyl.

Cycloalkyl-C₁- or -C₂-alkoxy radicals that are suitable as substituents are, for example, cyclopropyl-methoxy, cyclopropyl-ethoxy, cyclobutyl-methoxy, cyclobutyl-ethoxy, cyclopentyl-methoxy, cyclopentyl-ethoxy, cyclohexyl-methoxy and cyclohexyl-ethoxy.

Oxacycloalkyl radicals that are suitable as substituents are, for example, oxacyclobutyl, oxacyclopentyl, oxacyclohexyl and oxacycloheptyl, especially oxetan-3-yl, 3-methyl-oxetan-3-yl, 3-ethyl-oxetan-3-yl and 2-methyl-oxetan-3-yl.

Oxacycloalkyl-C₁-C₃alkyl radicals that are suitable as substituents are, for example, oxiran-2-yl-methyl, oxacyclobutyl-methyl, oxacyclobutyl-ethyl, oxacyclobutyl-propyl, oxacyclopentyl-methyl, oxacyclopentyl-ethyl, oxacyclopentyl-propyl, oxacyclohexyl-methyl, oxacyclohexyl-ethyl, oxacyclohexyl-propyl, oxacycloheptyl-methyl and oxacycloheptyl-propyl.

Dioxacycloalkyl radicals that are suitable as substituents are, for example, dioxacyclopentyl, dioxacyclohexyl, dioxacycloheptyl, methyldioxacyclopentyl, dimethyldioxacyclopentyl and dimethyldioxacyclohexyl.

Dioxacycloalkyl-C₁-C₃alkyl radicals that are suitable as substituents are, for example, dioxacyclopentyl-methyl, dioxacyclopentyl-ethyl, dioxacyclopentyl-propyl, dioxacyclohexyl-methyl, dioxacyclohexyl-ethyl, dioxacyclohexyl-propyl and dioxacycloheptyl-methyl, especially (1,3-dioxolan-2-yl)-methyl, (1,3-dioxolan-2-yl)-ethyl, (1,3-dioxan-2-yl)-ethyl and [1,3-(2,2-dimethyl)-dioxolan-5-yl]-methyl.

The invention also includes the salts that the compounds of formula I are capable of forming with amines, alkali metal and alkaline earth metal bases or quaternary ammonium bases.

Suitable salts of the free carboxy groups are especially salts of alkali metals, such as lithium, sodium and potassium, salts of alkaline earth metals, such as magnesium and calcium, or salts of organic ammonium bases, such as ammonia and primary, secondary and tertiary alkylamines.

Of the alkali metal and alkaline earth metal hydroxides, as salt formers, special mention should be made of the hydroxides of lithium, sodium, potassium, magnesium and calcium, but especially those of sodium and potassium.

Examples of amines that are suitable for the formation of ammonium salts include both ammonia and primary, secondary and tertiary C₁-C₁₈alkylamines, C₁-C₄hydroxyalkylamines and C₂-C₄alkoxyalkylamines, for example methylamine, ethylamine, n-propylamine, isopropylamine, the four isomers of butylamine, n-amylamine, isoamylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, methyl-ethylamine, methyl-isopropylamine, methyl-hexylamine, methyl-nonylamine, methyl-pentadecylamine, methyl-octa-

decylamine, ethyl-butylamine, ethyl-heptylamine, ethyl-octylamine, hexyl-heptylamine, hexyl-octylamine, dimethylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-butylamine, di-n-amylamine, diisoamylamine, dihexylamine, diheptylamine, dioctylamine, ethanolamine, n-propanolamine, isopropanolamine, N,N-diethanolamine, N-ethylpropanolamine, N-butylethanolamine, allylamine, n-butenyl-2-amine, n-pentenyl-2-amine, 2,3-dimethylbutenyl-2-amine, di-butenyl-2-amine, n-hexenyl-2-amine, propylenediamine, trimethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, tri-isobutylamine, tri-sec-butylamine, tri-n-amylamine, methoxyethylamine and ethoxyethylamine; heterocyclic amines, such as pyridine, quinoline, isoquinoline, morpholine, piperidine, pyrrolidine, indoline, quinuclidine, azepine and imidazole; primary arylamines, such as anilines, methoxyanilines, ethoxyanilines, o,m,p-toluidines, phenylenediamines, benzidines, naphthylamines and o,m,p-chloroanilines; but especially triethylamine, iso-propylamine and diisopropylamine.

When A and R together form a bond, a lactone structure as shown in compounds of formula I_r is obtained.

In preferred compounds of formula I, R₂ is hydrogen, methyl, methyl substituted by fluorine, chlorine or bromine, ethyl, pentafluoroethyl, phenyl, phenyl mono- to penta-substituted by fluorine and mono- or di-substituted by chlorine, bromine, trifluoromethyl or methoxy, pyridyl or thienyl.

Of those compounds, especially suitable are those compounds wherein R₂ is hydrogen, methyl, trifluoromethyl, chlorodifluoromethyl, dichlorofluoromethyl, dichloromethyl, tri-chloromethyl, dibromomethyl, ethyl, pentafluoroethyl, phenyl, phenyl mono-substituted by fluorine, chlorine, trifluoromethyl or methoxy, 2- or 3-pyridyl or 2-thienyl. Of those compounds of formula I very special preference is given to those wherein R₂ is methyl, trifluoromethyl, chlorodifluoromethyl, dichlorofluoromethyl, dichloromethyl or trichloromethyl.

Preference is given also to compounds of formula I wherein R₁ is C₁-C₃perhaloalkyl.

Of those compounds, preference is given especially to compounds of formula I wherein R₁ is trifluoromethyl, chlorodifluoromethyl, dichlorofluoromethyl, trichloromethyl, tribromo-methyl, pentafluoroethyl or heptafluoropropyl. Of those compounds of formula I very special preference is given to those wherein R₁ is trifluoromethyl.

Preference is given likewise to compounds of formula I wherein R₃ is methoxy; and R₄ is methyl, trifluoromethyl, chlorine, methoxy, difluoromethoxy, ethoxy or dimethylamino; or R₄ forms an -OCH₂CH₂- bridge to Z.

Of those compounds, compounds of formula I wherein R₃ and R₄ are methoxy are especially important.

Also preferred are those compounds of formula I wherein Z is methine.

Also suitable are compounds of formula I wherein R₃ and R₄ are methoxy; and Z is methine.

Also important are compounds of formula I wherein R is C₁-C₄alkyl, 2-propenyl, 2-propynyl, 2-fluoroethyl, 2-chloroethyl, 2-methoxyethyl, 2-cyanoethyl or benzyl.

Of those compounds, compounds of formula I wherein R is methyl or ethyl are especially important.

Suitable compounds are also those wherein R is hydrogen.

Also suitable are compounds wherein A and R together form a bond.

Also suitable are compounds of formula I wherein

A is hydroxy, C₁-C₄alkoxy, 2-propenyoxy, 2-propynyloxy, benzyloxy, C₁-C₄alkylcarbonyloxy-C₁- or -C₂-alkoxy, N,N-dimethylhydroxyamino, N-methoxyamino, cyanamino, or a group of the formula A₁, A₂, A₃ or A₄, wherein

R₈ is a -COL group and

L is as defined for formula I;

R₇ is hydrogen;

R₉ is hydrogen or C₁-C₄alkyl; or

R₇ and R₉ together are -(CH₂)₃-;

R₁₀ is hydrogen;

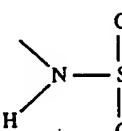
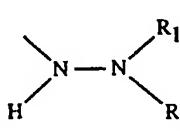
R₁₁ is C₁-C₄alkyl, cyclopropylmethyl, C₃- or C₄-alkenyl, C₃- or C₄-haloalkenyl, cyclopropyl, cyclobutyl, trifluoromethyl, ethylamino, n-propylamino, 2-propynylamino, di-C₁-C₄alkylamino, morpholino, pyridyl or pyridyl substituted by halogen or by

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methoxycarbonyl, N-methoxy-methylamino, phenyl or phenyl mono- or di-substituted by fluorine, chlorine, bromine or methoxy; and

R_{13} is hydrogen, C_1 - C_4 alkyl, phenyl or phenyl mono- or di-substituted by fluorine, chlorine, methyl, trifluoromethyl, methoxy, methoxycarbonyl or nitro.

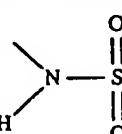
Especially suitable are compounds of formula I wherein A is hydroxy or a group of the

formula  R_{11} (A₃) or  R_{12} (A₄) wherein R_{11} to R_{13} are as

defined for formula I.

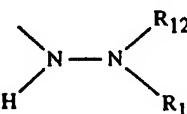
Especially important are compounds of formula I wherein A is hydroxy.

Also especially suitable are compounds of formula I wherein A is a group of the formula

 R_{11} (A₃) wherein R_{11} is methyl, ethyl, trifluoromethyl, 2-methyl-

2-propenyl, 3-chloro-2-propenyl, cyclopropyl, cyclopropylmethyl, dimethylamino, diethylamino, morpholino, phenyl, 2-chlorophenyl, 2-methoxycarbonylphenyl, 2-pyridyl, 3-fluoro-2-pyridyl or 3-methoxycarbonyl-2-pyridyl.

Also especially suitable are compounds of formula I wherein A is a group of the formula

 R_{12} (A₄) wherein R_{12} is hydrogen; and R_{13} is methyl, tert-butyl, phenyl,

2-chlorophenyl, 2-fluorophenyl, 2,4-difluorophenyl, 2-tolyl, 4-methoxyphenyl, 4-chlorophenyl or 3-trifluoromethylphenyl.

Also suitable are compounds of formula I wherein A is a group of the formula

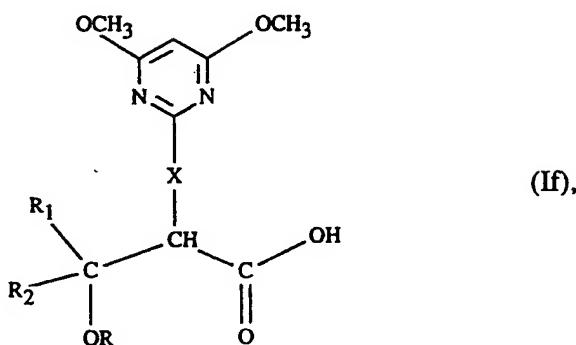
 R_7 R_8 R_9 (A₁*) of (S)-configuration; R_7 is hydrogen; R_9 is C_1 - C_4 alkyl; or R_7

and R_9 together are $-(CH_2)_3-$; and R_8 is a -COL group wherein L is as defined for

- 11 -

formula I.

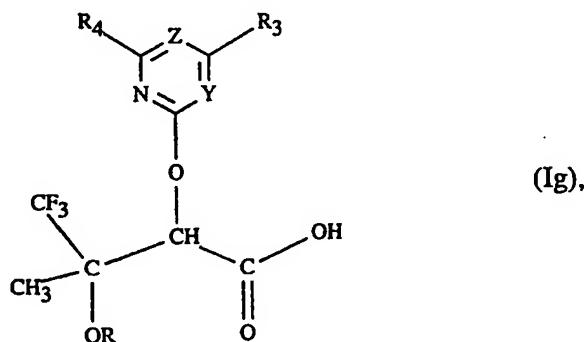
Importance is attached to those compounds of formula If



wherein

- R is hydrogen, methyl, ethyl, difluoromethyl, 2-fluoroethyl, 2-chloroethyl, 2-cyanoethyl, 2-methoxyethyl, 2-ethoxyethyl, n-propyl, 2-propenyl, 2-propynyl or benzyl;
- R₁ is trifluoromethyl, chlorodifluoromethyl, trichloromethyl, tribromomethyl, pentafluoroethyl or heptafluoropropyl; and
- R₂ is hydrogen, methyl, trifluoromethyl, chlorodifluoromethyl, dichlorofluoromethyl, dichloromethyl, trichloromethyl, dibromomethyl, ethyl, pentafluoroethyl, phenyl, phenyl mono-substituted by fluorine, chlorine, trifluoromethyl or methoxy, 2- or 3-pyridyl or 2-thienyl.

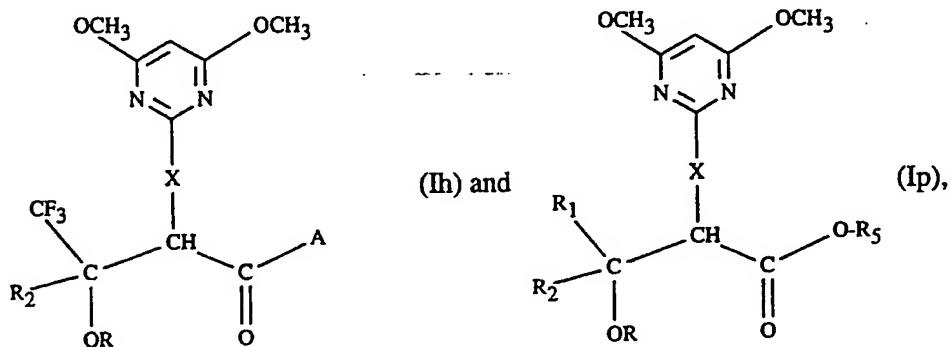
Also important are those compounds of formula Ig



wherein

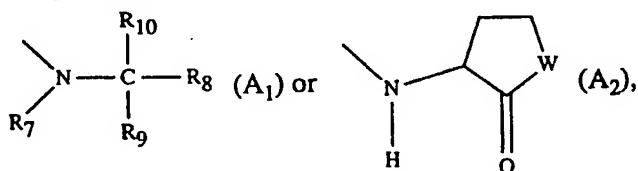
R is methyl, ethyl, difluoromethyl, 2-fluoroethyl, 2-chloroethyl, 2-methoxyethyl, 2-ethoxyethyl, n-propyl, 2-propenyl, 2-propynyl, 2-cyanoethyl or benzyl;
 R₃ is methoxy or ethoxy;
 R₄ is methyl, trifluoromethyl, trichloromethyl, methoxy, difluoromethoxy, methylamino, dimethylamino, methylthio or cyclopropyl;
 Y is nitrogen, methine or chloromethine; and
 Z is nitrogen or methine; or
 R₄ forms a -O(CH₂)₂- bridge to Z.

Also suitable are those compounds of formulae I_h and I_p



wherein

R is hydrogen, methyl, ethyl, difluoromethyl, 2-fluoroethyl, 2-chloroethyl, 2-cyanoethyl, 2-methoxyethyl, 2-ethoxyethyl, n-propyl, 2-propenyl, 2-propynyl or benzyl;
 R₂ is methyl, trifluoromethyl or phenyl;
 A is methoxy, ethoxy, tert-butoxy, 2-propenyl, 2-propynyl, 2-propenylideneiminoethoxy, N,N-di-methylaminoxy, methoxyamino, cyanamino, imidazolyl or a group of the formula



wherein

R₇ is hydrogen;
 R₉ is hydrogen, C₁-C₄alkyl or C₁-C₄alkyl substituted by carboxy, phenyl, methylphosphino or methylthio; or

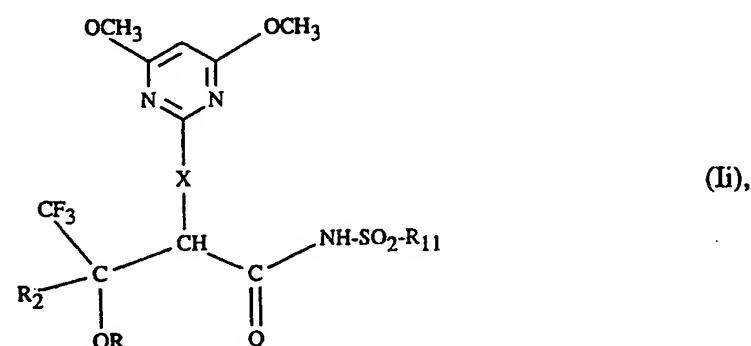
- 13 -

R_7 and R_9 together are $-(CH_2)_3-$;

R_8 is methylphosphino or a $-COL$ group, and L is hydroxy or C_1-C_4 alkoxy; and

R_{10} is hydrogen.

Preference is given also to compounds of formula II



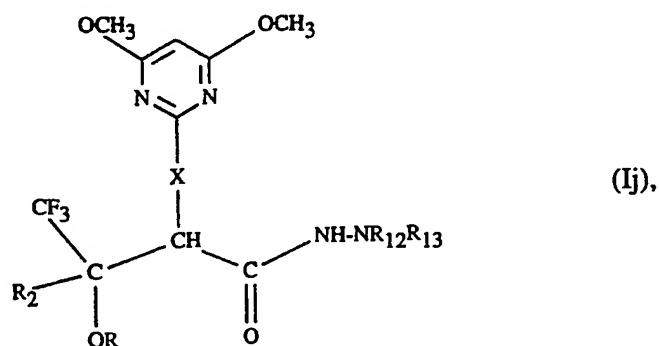
wherein

R is hydrogen, methyl, ethyl, difluoromethyl, 2-fluoroethyl, 2-chloroethyl, 2-cyanoethyl, 2-methoxyethyl, 2-ethoxyethyl, n-propyl, 2-propenyl, 2-propynyl or benzyl;

R_2 is methyl or trifluoromethyl; and

R_{11} is methyl, ethyl, trifluoromethyl, 2-methyl-2-propenyl, 3-chloro-2-propenyl, cyclopropyl, dimethylamino, diethylamino, morpholino, phenyl, 2-chlorophenyl, 2-methoxycarbonylphenyl, 2-pyridyl, 3-fluoro-2-pyridyl or 2-fluoro-3-pyridyl.

Preference is given also to those compounds of formula Ij



wherein

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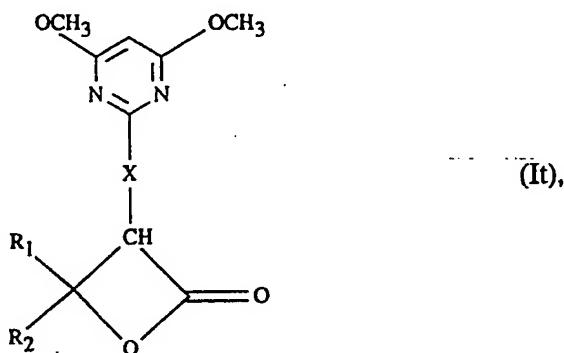
R is hydrogen, methyl, ethyl, difluoromethyl, 2-fluoroethyl, 2-chloroethyl, 2-methoxyethyl, 2-ethoxyethyl, n-propyl, 2-propenyl, 2-propynyl, 2-cyanoethyl or benzyl;

R₂ is methyl, trifluoromethyl or phenyl;

R₁₂ is hydrogen or methyl; and

R₁₃ is methyl, tert-butyl, phenyl, 2-chlorophenyl, 2-fluorophenyl, 2-tolyl, 2,4-difluorophenyl, 4-chlorophenyl, 3-trifluoromethylphenyl or 4-methoxyphenyl.

Preference is given also to those compounds of formula I



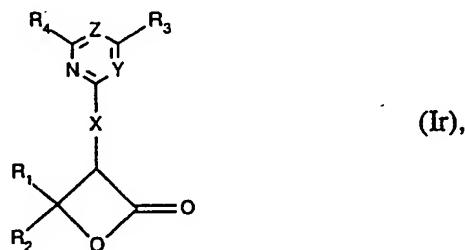
wherein

X is oxygen or sulfur;

R₁ is trifluoromethyl, pentafluoroethyl or heptafluoropropyl; and

R₂ is methyl, ethyl, trifluoromethyl or phenyl.

Preference is likewise given to compounds of formula I



wherein

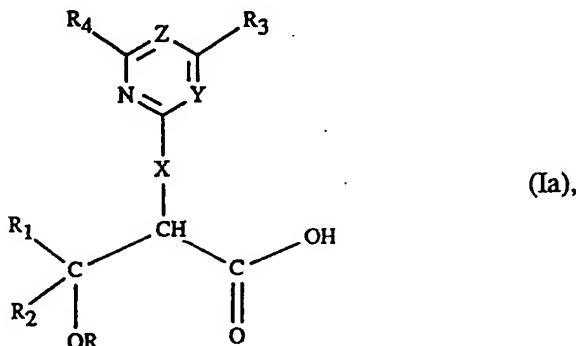
R₂ to R₄, X, Y and Z are as defined for formula I and R₁ is C₁-C₇alkyl, or R₁ together with R₂ is -(CH₂)₄- or -(CH₂)₅-.

There may be mentioned as very especially preferred individual compounds within the

scope of formula I, in the form of a mixture of stereoisomers or in the form of pure isomers:

2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3-trifluoromethylbutyric acid;
 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-hydroxy-3-trifluoromethylbutyric acid;
 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-ethoxy-3-trifluoromethylbutyric acid;
 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methyl-3-trifluoromethyl-oxetanone;
 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-methoxy-3-trifluoromethylbutyric acid;
 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-ethoxy-3-trifluoromethylbutyric acid;
 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3,3-bis-trifluoromethylpropionic acid;
 and
 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-hydroxy-3,3-bis-trifluoromethylpropionic acid.

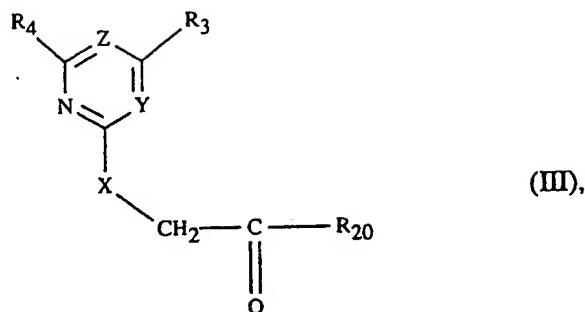
The process according to the invention for the preparation of the compounds of formula I is carried out analogously to known processes and comprises, for the preparation of the acid derivatives of formula Ia



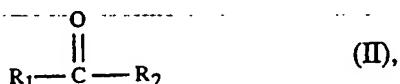
wherein R₁ to R₄, X, Y and Z are as defined for formula I and R is C₁-C₆alkyl, C₁-C₄halo-alkyl, C₁- or C₂-alkyl substituted by C₁- or C₂-alkoxy, cyano, phenyl or phenyl substituted by halogen, methyl, methoxy or trifluoromethyl, C₃-C₆alkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl-C₁- or -C₂-alkyl, C₄-C₆cycloalkyl, C₁-C₄alkylcarbonyl or C₁-C₄alkylsulfonyl,

a) converting a compound of formula III

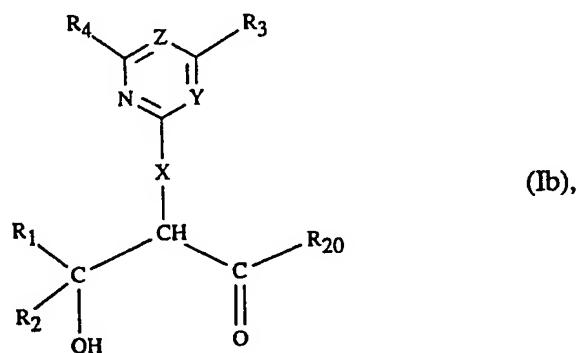
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wherein R_3 , R_4 , X , Y and Z are as defined and R_{20} is C_1-C_6 alkoxy, chloroethoxy, 2-trimethylsilylethoxy, 2-propenylxy, benzyloxy or benzyloxy substituted by methoxy, with a compound of formula II



wherein R_1 and R_2 are as defined, in the presence of a suitable base into a compound of formula Ib

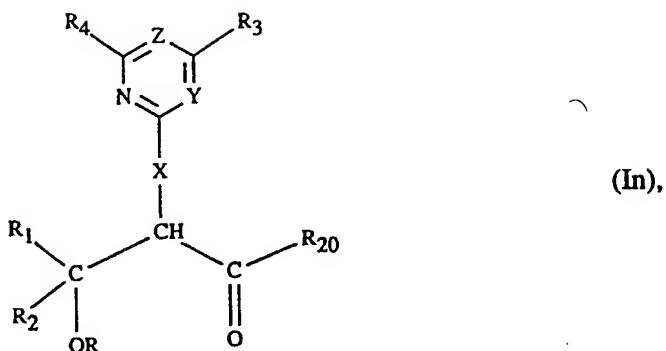


wherein R_1 to R_4 , X , Y , Z and R_{20} are as defined, and then alkylating, acylating or sulfonylating the compound of formula Ib with a compound of formula IX



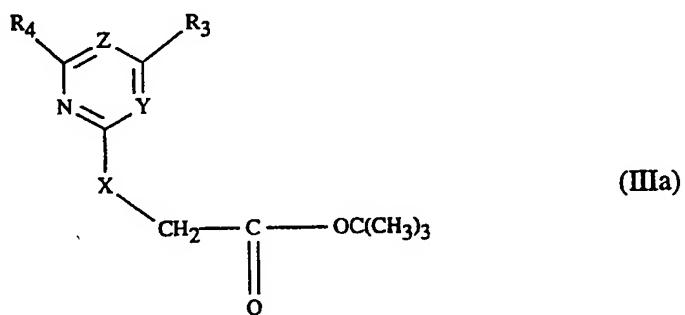
wherein R is as defined and L_5 is a leaving group, especially chlorine, bromine, iodine or a methylsulfonyloxy, p-toluenesulfonyloxy, methoxysulfonyloxy or ethoxysulfonyloxy group, to form the compound of formula In

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wherein R, R₁ to R₄, R₂₀, X, Y and Z are as defined, where appropriate in the presence of a base and a suitable solvent, and then reacting that compound of formula In further under hydrolytic or hydrogenolytic conditions or, when R₂₀ is the tert-C₄H₉-O- group, under acid-catalysed conditions; or

b) reacting a compound of formula IIIa

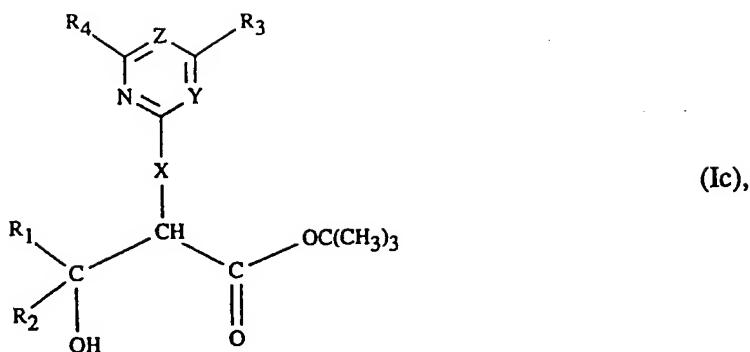


with a compound of formula II



in the presence of a suitable base, to form a compound of formula Ic

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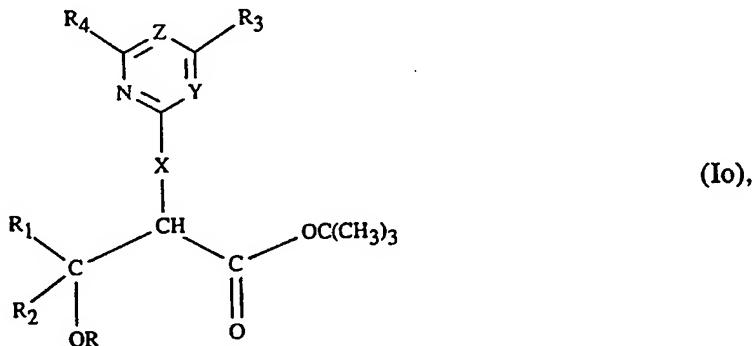


(Ic),

wherein in the compounds of formulae IIIa, II and Ic the radicals R_1 to R_4 , X , Y and Z are as defined for formula I, and then alkylating, acylating or sulfonylating the compound of formula Ic with a compound of formula IX

$R-L_5$ (IX),

wherein R is as defined and L_5 is a leaving group, especially chlorine, bromine, iodine or a methylsulfonyloxy, p-toluenesulfonyloxy, methoxysulfonyloxy or ethoxysulfonyloxy group, where appropriate in the presence of a base and a suitable solvent, to form a compound of formula Io

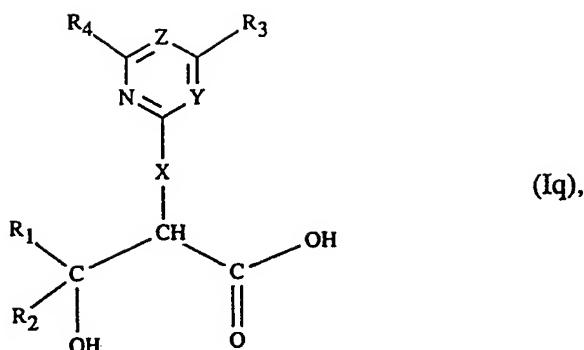


(Io),

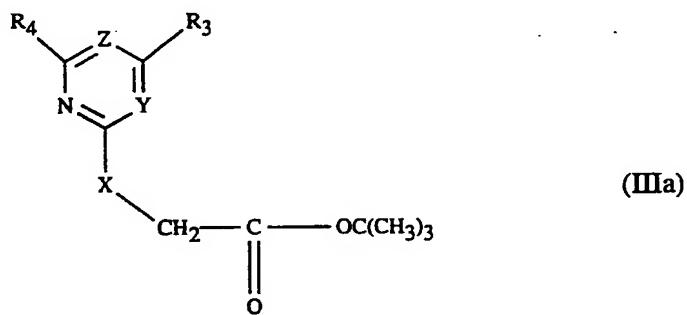
and then hydrolysing the compound of formula Io with trifluoroacetic acid, sulfuric acid or a mixture of sulfuric acid and acetic acid, where appropriate in the presence of an additional solvent.

The process according to the invention for the preparation of the acid derivatives of formula Iq

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wherein R₂ to R₄, X, Y and Z are as defined for formula I and R₁ is C₁-C₇alkyl or C₁-C₇haloalkyl, or R₁ together with R₂ is -(CH₂)₄- or -(CH₂)₅-, comprises reacting a compound of formula IIIa

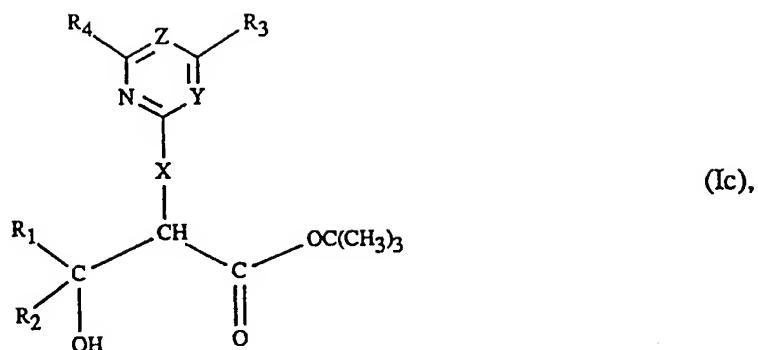


with a compound of formula II



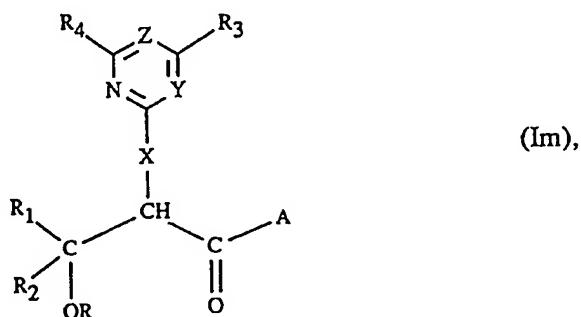
in the presence of a suitable base, to form a compound of formula Ic

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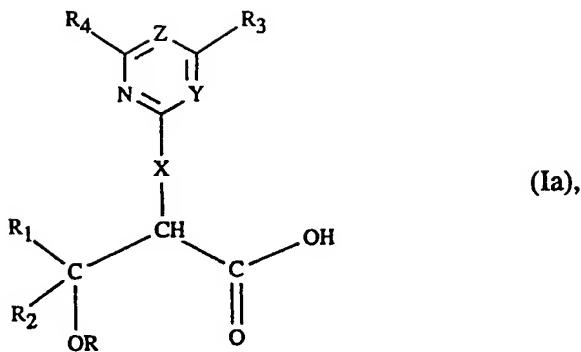
wherein in the compounds of formulae IIIa, II and Ic the radicals R₂ to R₄, X, Y and Z are as defined for formula I and R₁ is C₁-C₇alkyl or C₁-C₇haloalkyl, or R₁ together with R₂ is -(CH₂)₄- or -(CH₂)₅-, and then hydrolysing the compound of formula Ic with trifluoroacetic acid, sulfuric acid, phosphoric acid or a mixture of sulfuric acid and acetic acid, where appropriate in the presence of an additional solvent.

The process according to the invention for the preparation of the compounds of formula Im



wherein R₁ to R₄, X, Y and Z are as defined for formula I, R is C₁-C₆alkyl, C₁-C₄haloalkyl, C₁- or C₂-alkyl substituted by C₁- or C₂-alkoxy, cyano, phenyl or phenyl substituted by halogen, methyl, methoxy or trifluoromethyl, C₃-C₆alkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl-C₁- or -C₂-alkyl, C₄-C₆cycloalkyl, C₁-C₄alkylcarbonyl or C₁-C₄alkylsulfonyl and A is -OR₅, -SR₆, cyanamino or a group A₁ to A₄, comprises converting a compound of formula Ia

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wherein R, R₁ to R₄, X, Y and Z are as defined,

a) by reaction with a compound of formula VII



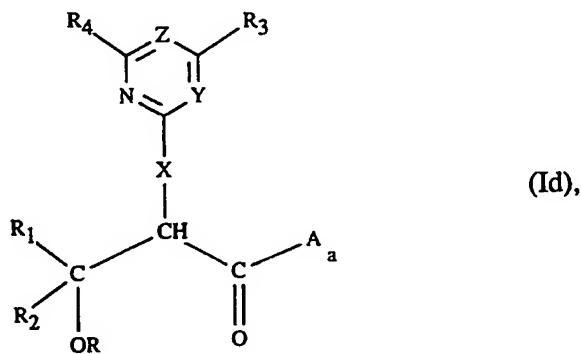
wherein

A_a is a leaving group, especially chlorine, bromine, 2,4,6-triisopropylphenyl-sulfonyl,

imidazolyl, triazolyl, 2-thionothiazolidin-3-yl or N,N'-dicyclohexyl-isoureidyl, and

L_3 is -S(O)Cl, -C(O)Cl, -C(O)-C(O)Cl, -PCl₄, -P(O)Cl₂, -P(O)Br₂, 2,4,6-triisopropyl-phenyl-sulfonyl, imidazolyl, triazolyl, N-carbonylimidazole or N-carbonyltriazole,

into the compound of formula Id

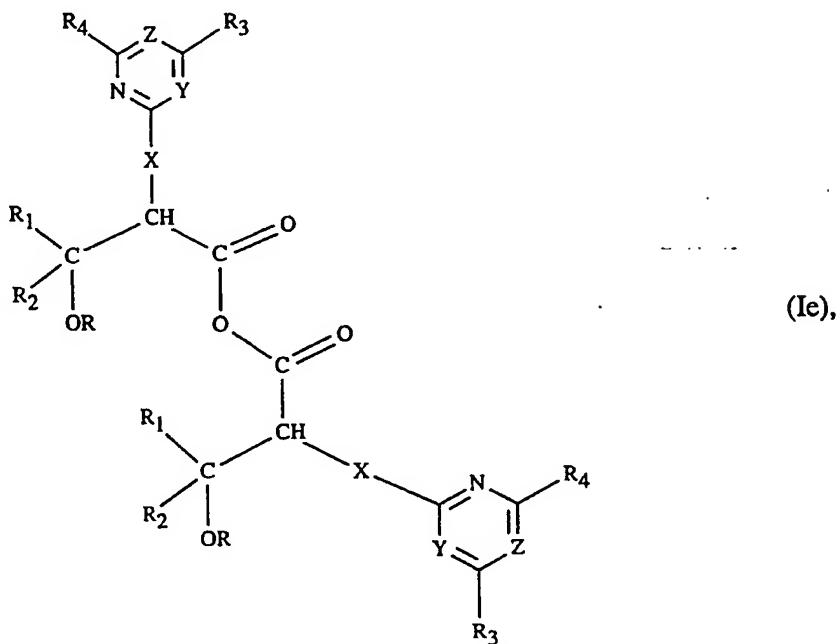


wherein R₁ to R₄, X, Y and Z are as defined for formula I and R and A_a are as defined above, and then reacting the compound of formula Id with a compound of formula V



wherein A is -OR₅, -SR₆, cyanamino or a group A₁ to A₄, where appropriate in the presence of a base and a solvent; or

b) by treatment with a water-removing reagent, such as phosphorus oxychloride, into the compound of formula Ie



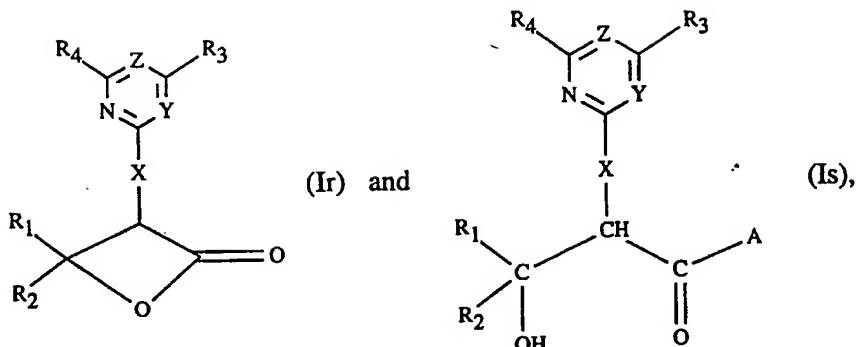
wherein R₁ to R₄, X, Y and Z are as defined for formula I and R is as defined above, and then reacting the compound of formula Ie with a compound of formula V

A-H (V),

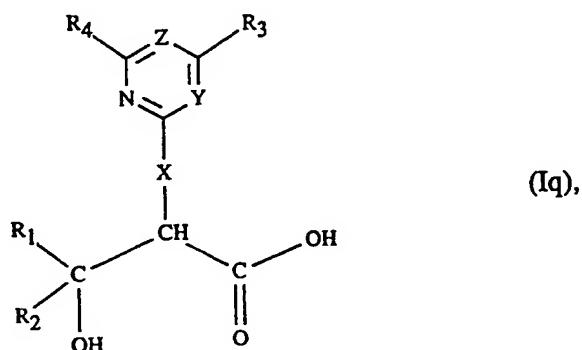
wherein A is -OR₅, -SR₆, cyanamino, hydroxyamino, C₁-C₆alkoxyamino, C₁-C₃alkoxy-(C₁-C₃alkyl)amino or a group A₁ to A₄, where appropriate in the presence of a base and a solvent.

The process according to the invention for the preparation of the compounds of formulae I_r and I_s

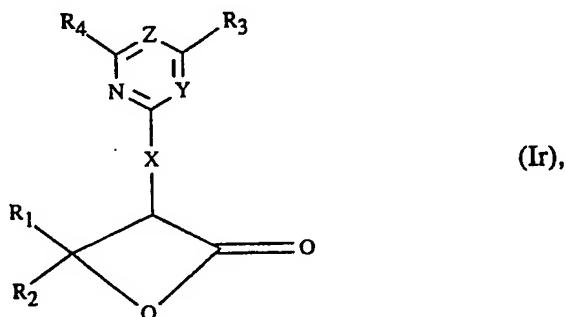
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wherein R₂ to R₄, X, Y, Z and A are as defined for formula I and R₁ is C₁-C₇alkyl or C₁-C₇haloalkyl, or R₁ together with R₂ is -(CH₂)₄- or -(CH₂)₅-, comprises converting a compound of formula Iq



wherein R₁ to R₄, X, Y and Z are as defined, by treatment with a water-removing reagent, such as phosphorus oxychloride, phosphorus trichloride, phosphorus pentachloride, phosphorus oxybromide, thionyl chloride, oxalyl chloride, acetic anhydride, sulfuric acid, dimethyl- or diethyl-amino sulfur trifluoride, into the compound of formula Ir

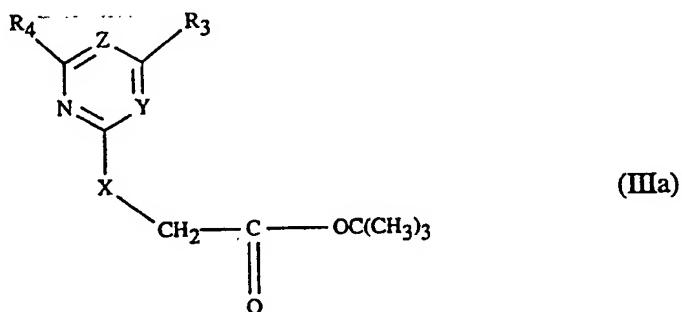


wherein R₂ to R₄, X, Y and Z are as defined for formula I and R₁ is C₁-C₇alkyl or C₁-C₇haloalkyl, or R₁ together with R₂ is -(CH₂)₄- or -(CH₂)₅- , and then reacting the compound of formula I_r with a compound of formula V

A-H (V),

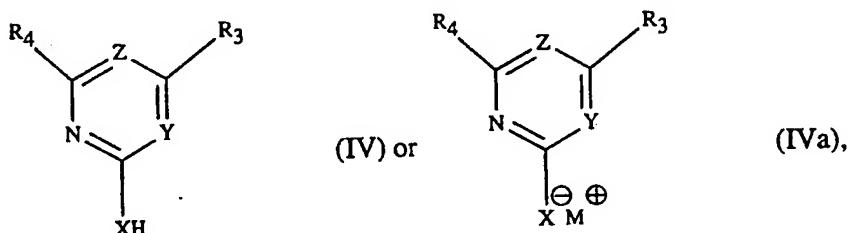
wherein A is hydroxy, -OR₅, -SR₆, cyanamino, hydroxyamino, C₁-C₆alkoxyamino, C₁-C₃alkoxy-C₁-C₆alkylamino or a group A₁ to A₄ , where appropriate in the presence of a base and a solvent.

Compounds of formula IIIa



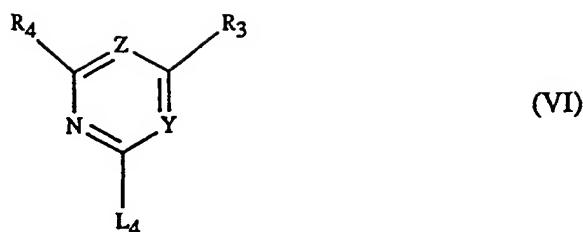
wherein R₃, R₄, X, Y and Z are as defined for formula I can be prepared by

a) reacting a compound of formula IV or IVa



wherein M[⊕] is a cation, such as a sodium, calcium, lithium, magnesium, dimethylammonium or triethylammonium ion, with bromo- or chloro-acetic acid tert-butyl ester in the presence of a base and a suitable solvent; or

b) reacting a compound of formula VI



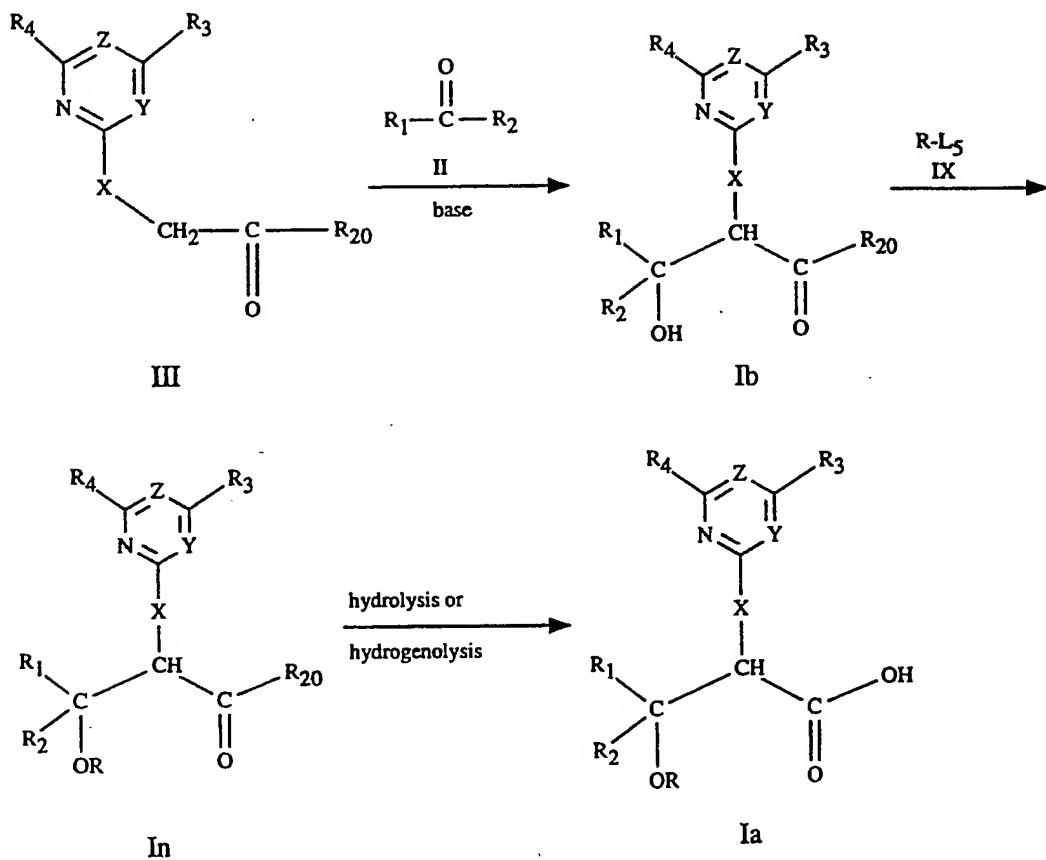
with hydroxy- or mercapto-acetic acid *tert*-butyl ester (VIII) in the presence of a base and a suitable solvent; in the compounds of formulae IV and VI the radicals R₃, R₄, X, Y and Z are as defined for formula I and L₄ is a leaving group, such as fluorine, chlorine, methylsulfonyl or benzylsulfonyl.

The process variants for the preparation of the acid derivatives of formula Ia wherein R is C₁-C₆alkyl, C₁-C₄haloalkyl, C₁- or C₂-alkyl substituted by C₁- or C₂-alkoxy, cyano, phenyl or phenyl substituted by halogen, methyl, methoxy or trifluoromethyl, C₃-C₆alkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl-C₁- or -C₂-alkyl, C₄-C₆cycloalkyl, C₁-C₄alkylcarbonyl or C₁-C₄alkylsulfonyl, follow Reaction scheme 1, the preparation of acid derivatives of formulae Ia and Iq wherein R is hydrogen advantageously being effected using Process variant 1b) *via* the acid-catalysed removal of isobutylene (see Reaction scheme 3). The process variant for the preparation of the compounds of formula Im wherein A is -OR₅, -SR₆, cyanamino, hydroxyamino, C₁-C₆alkoxyamino, C₁-C₃alkoxy-C₁-C₃alkylamino or a group A₁ to A₄, and R has the meanings given, with the exception of hydrogen, follows Reaction scheme 2; the process variant for the preparation of compounds of formulae Iq, Ir and Is (and Im wherein R is hydrogen) wherein the radical R₁ is C₁-C₇alkyl or C₁-C₇haloalkyl, or R₁ together with R₂ is -(CH₂)₄- or -(CH₂)₅-, and the radicals R₂ to R₄, X, Y, Z and A are as defined, follows Reaction scheme 3, and the process variants for the preparation of the novel intermediates of formula IIIa follow Reaction scheme 4.

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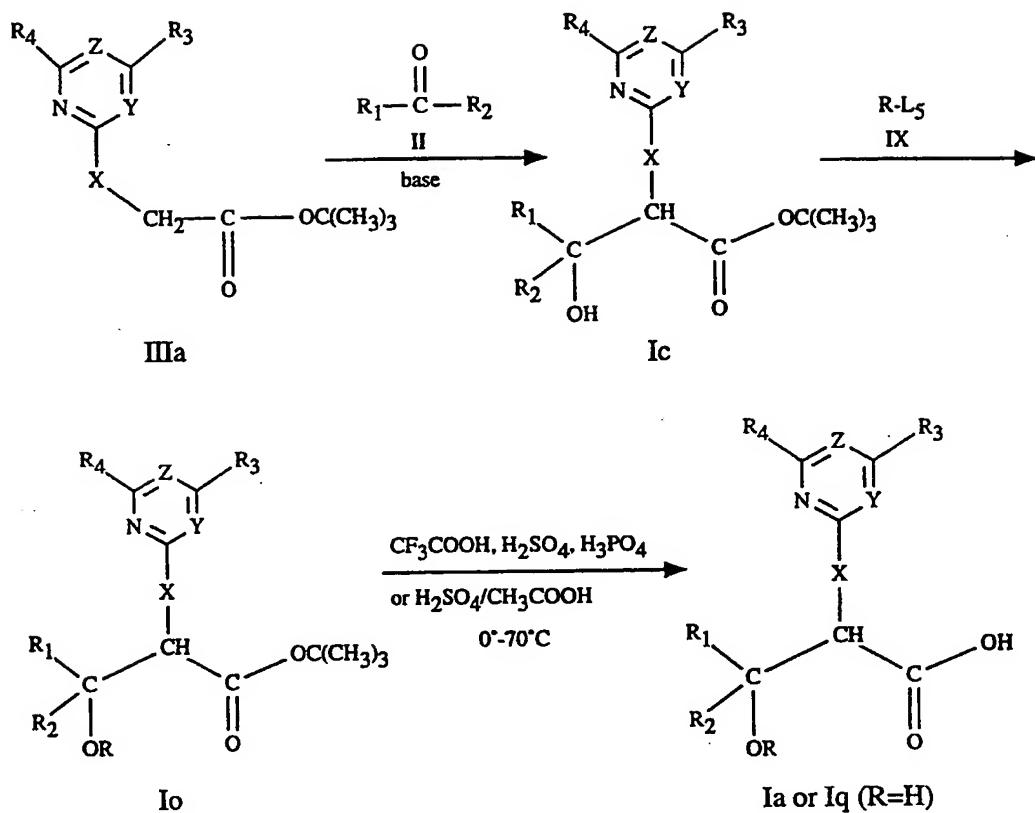
Reaction scheme 1:

Route a):

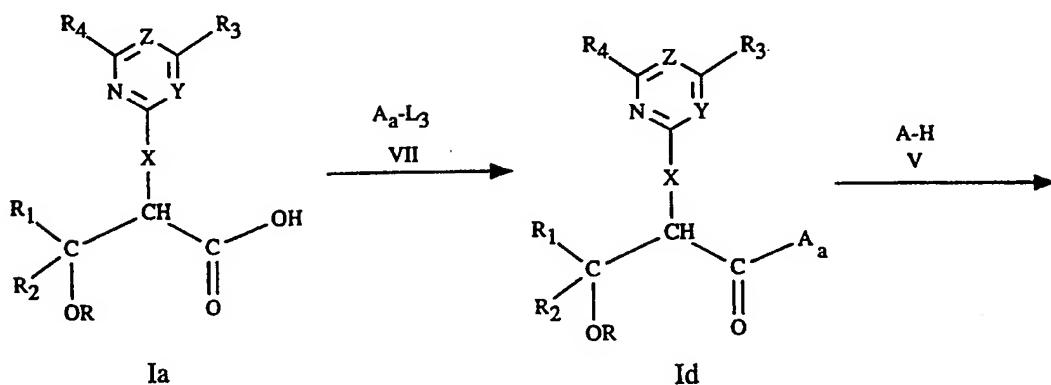


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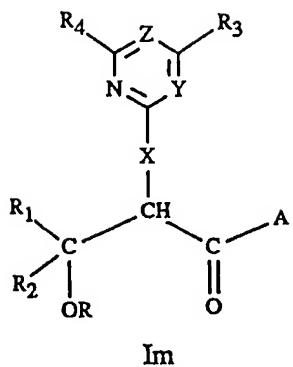
Route b):

Reaction scheme 2:

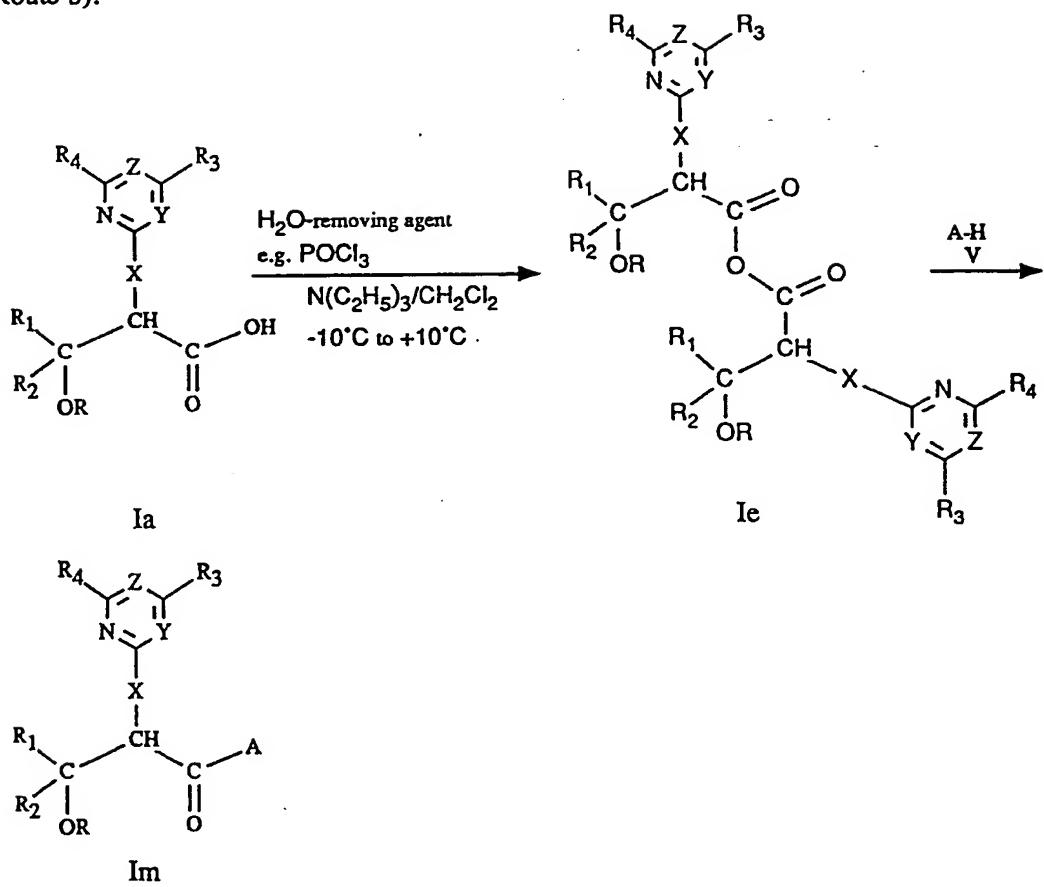
Route a):



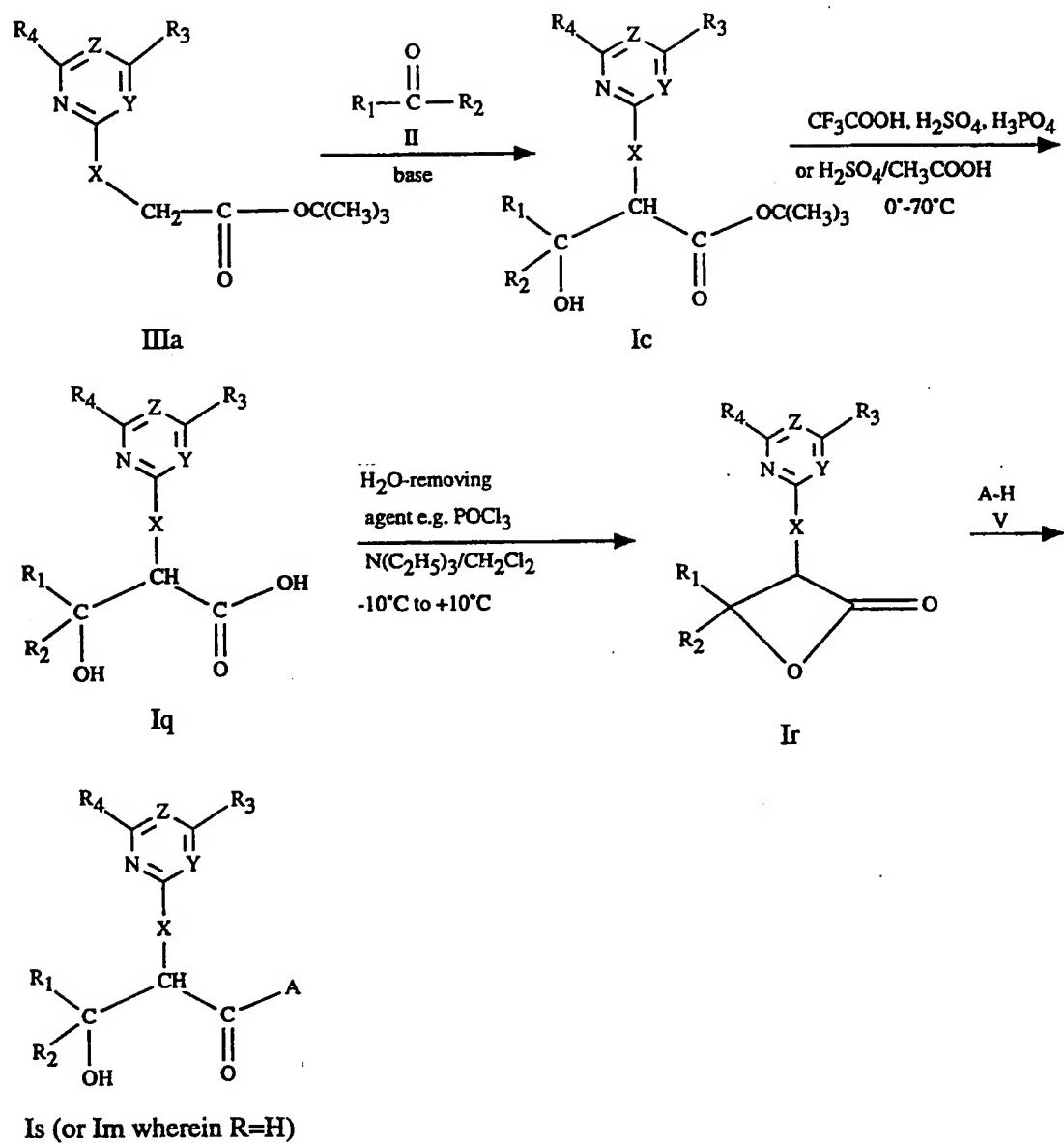
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Route b):

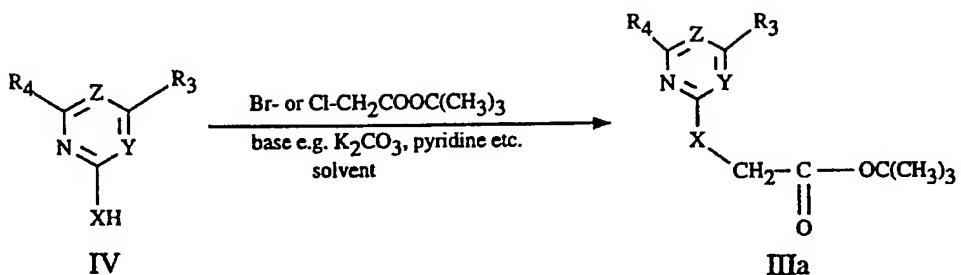


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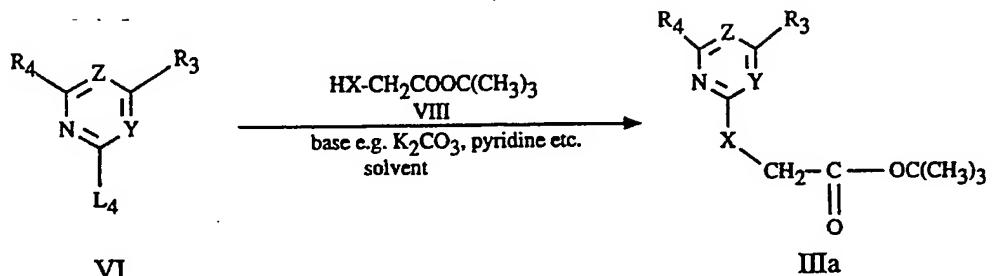
Reaction scheme 3:

Reaction scheme 4:

Route a):



Route b):



The condensation reaction of the compounds of formulae III and IIIa with compounds of formula II in accordance with Reaction scheme 1 can advantageously be carried out in the presence of a strong base, such as lithium diisopropylamide, a potassium, sodium or lithium salt of hexamethyldisilazane, n-butyllithium, sec-butyllithium, tert-butyllithium or phenyllithium in hexane, heptane, diethoxymethane, isooctane, diethyl ether or tetrahydrofuran, especially with bis(trimethylsilyl)lithium amide in hexane and/or tetrahydrofuran, in accordance with processes known *per se* at temperatures of from -78°C to 0°C, preferably at temperatures of from -70°C to -50°C, in one of the solvents mentioned above and analogously to EP-A-0 409 368, EP-A-0 517 215, Japanese Patent 04 342 573 and J. Org. Chem. 54, 1543 (1989). There may be obtained an isomeric mixture of compounds of formula Ib or Ic or alternatively, depending upon the substituents R₁, R₂, X, R₂₀ and -OC(CH₃)₃ and the reaction conditions used, a concentration of one or other isomeric form may be obtained preferentially. The isomeric mixture of compounds of formula Ib or Ic can be separated by known methods, for example by means of column chromatography or by fractional crystallisation with the aid of a suitable solvent.

Compounds of formula In or Io wherein R has the meaning given above, with the exception of hydrogen, can be prepared by reacting the intermediate of formula Ib or Ic with the corresponding electrophilic compound of formula IX in the presence of a base, such as sodium hydride, potassium hydride, lithium diisopropylamide, tetramethylethylene-diamine, triethylamine, 4-dimethylaminopyridine or diisopropylethylamine, in the presence of a suitable solvent, such as the solvents indicated above, or N,N-dimethylformamide, N-methylpyrrolidone, acetonitrile, toluene, dimethyl sulfoxide or a mixture thereof. The reaction is carried out at from -50°C to the boiling temperature of the reaction mixture, preferably from 0°C to 80°C. Suitable alkylating agents of formula IX are, especially for the preparation of compounds of formula I wherein R is methyl or ethyl, dimethyl sulfate and diethyl sulfate.

Advantageously, the reaction of III to In or IIIa to Io can be carried out directly *in situ* without isolation of the intermediates of formula Ib or Ic, respectively. In that case, the lithium, sodium or potassium salt obtained as intermediate at temperatures of from -78°C to 0°C during the reaction of III to Ib or IIIa to Ic is combined directly at temperatures of from -50°C to 0°C with the electrophilic compound of formula IX and then, if necessary, the reaction mixture can be heated until the reaction is complete. The resulting isomeric mixture of formula In or Io can be separated by known methods, such as column chromatography or fractional crystallisation.

Compounds of formula In wherein R₂₀ is C₁-C₆alkoxy, chloroethoxy, 2-trimethylsilyl-ethoxy, 2-propenoxy, benzyloxy or benzyloxy substituted by methoxy, can be converted analogously to known processes, such as those described, for example, in EP-A-0 347 811, EP-A-0 400 741, EP-A-0 409 368, EP-A-0 481 512 and EP-A-0 517 215, by hydrolysis or hydrogenolysis into the acids of formula Ia in accordance with Reaction scheme 1, Route a). Suitable hydrolysing agents are, for example, sodium and potassium hydroxide or sodium and potassium carbonate. Tris(triphenylphosphine)-rhodium(I) chloride (Wilkinson catalyst) is suitable as hydrolysing agent, for example, where R₂₀ is 2-propenoxy, and hydrogen in the presence of a palladium/carbon catalyst is suitable as hydrolysing agent where R₂₀ is benzyloxy. Suitable solvents for the hydrolysis are, for example, water or mixtures of methanol/water, ethanol/water, tetrahydrofuran/water, diethoxymethane/water, dioxane/water or N,N-dimethylformamide/water. Suitable solvents for the hydrogenolysis are especially methanol, ethanol, ethyl acetate, acetic acid, trifluoroacetic acid, dioxane and water, and mixtures thereof.

Some of those known hydrolysis and hydrogenolysis processes, however, yield the acid of formula Ia, if at all, only in poor yields and with an insufficient degree of purity.

It has been found that hydrolysis of the compounds of formula Io (wherein R_{20} is $-OC(CH_3)_3$) produces the desired acid of formula Ia very readily in a good yield and with a high degree of purity with trifluoroacetic acid, phosphoric acid, sulfuric acid or a mixture of sulfuric acid and acetic acid and, where appropriate, in the presence of an additional solvent, such as dichloromethane, n-hexane, toluene or dioxane, in accordance with Reaction scheme 1, Route b). In that process it is advantageous to work with a slight excess of trifluoroacetic acid and without an additional solvent at mild temperatures of approx. from 0°C to 25°C or at slightly elevated temperatures of up to approx. 70°C. When trifluoroacetic acid is used as reaction medium, the excess trifluoroacetic acid can subsequently be evaporated off *in vacuo*.

Compounds of formula Im wherein A is $-OR_5$, $-SR_6$, cyanamino, hydroxy, C_1-C_6 alkoxy-amino, C_1-C_3 alkoxy(C_1-C_3 alkyl)amino or a group A₁ to A₄ can be prepared, for example, by reacting an acid of formula Ia with a chlorinating agent A_a-L₃ (VII), such as phosphorus oxychloride, thionyl chloride, oxalyl chloride or phosgene, phosphorus pentachloride or phosphorus oxybromide, especially phosphorus oxychloride, in the presence of a base, such as triethylamine, N,N-dimethylaniline or pyridine, and where appropriate in a solvent, such as a hydrocarbon, for example toluene, a chlorinated hydrocarbon, for example methylene chloride, or an ether, for example tetrahydrofuran, in a temperature range of from -20°C to the reflux temperature of the reaction mixture, preferably at from -5°C to 25°C, to form a compound of formula Id wherein A_a is chlorine or bromine, and reacting the corresponding acid chloride (wherein A_a is chlorine), also without isolation, directly with the corresponding nucleophilic compound of formula V, where appropriate in the presence of an additional base, especially a tertiary amine, such as triethylamine, N,N-dimethylaniline, 1,8-diazabicyclo[5.4.0]undec-7-ene, imidazole, pyridine or 2,5-dimethylpyridine, in accordance with Reaction scheme 2. The base can be used in a catalytic amount or in a stoichiometric amount or in excess, preferably in a stoichiometric amount or a slight excess. It is also possible to use as the base a slight excess, such as 2 equivalents, of the substrate of formula V used.

The reaction is preferably carried out also in the presence of a suitable solvent, for example a hydrocarbon, such as toluene; a halogenated hydrocarbon, such as dichloro-

methane, 1,2-dichloroethane or chlorobenzene; an ether, such as diethyl ether, diethoxy-methane or tert-butyl methyl ether; an ester, such as ethyl acetate; an aprotic solvent, such as acetonitrile; a protic solvent, such as ethanol or water; or a two-phase system, such as a mixture of dichloromethane/water, toluene/water, ethyl acetate/water or tert-butyl methyl ether/water. The reaction temperatures may be varied within a wide range of approximately from -40°C to the boiling temperature of the solvent used. The reaction is preferably carried out, however, at temperatures of from -20°C to approx. +30°C, especially from -10°C to +10°C. The reaction times may, however, vary widely according to the temperature of the reaction mixture and the base used.

Compounds of formula Id wherein A_a is a leaving group, such as 2,4,6-triisopropyl-phenyl-sulfonyl, imidazolyl, triazolyl, 2-thiono-thiazolidin-3-yl or N,N'-dicyclohexyl-isoureidyl, can likewise be prepared from compounds of formula Ia in accordance with known conversion processes using 1-(2,4,6-triisopropylphenyl-sulfonyl)-imidazole as described in Tetrahedron Lett. 1973, 1353, using 1-(2,4,6-triisopropylphenyl-sulfonyl)-1H-1,2,4-triazole as described in Chem. Commun. 1974, 325, using 1,1'-carbonyl-diimidazole or 1,1'-carbonyl-di(1,2,4-triazole) as described in Angew. Chem. 74, 407 (1962), using thiazolidine-2-thione as described in Tetrahedron Lett. 21, 841 (1980), or using dicyclohexylcarbodiimide. In those cases also, the intermediates of formula Id can be reacted directly with the nucleophilic compound of formula V without being isolated.

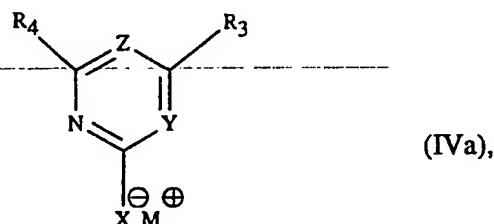
It has now been found that the hydrolysis of the compounds of formula Ic (wherein R_{20} is $-\text{OC}(\text{CH}_3)_3$) produces the desired acid of formula Iq very readily in a good yield and with a high degree of purity with trifluoroacetic acid, sulfuric acid, phosphoric acid or a mixture of sulfuric acid and acetic acid, where appropriate in the presence of an additional solvent, such as dichloromethane, n-hexane, toluene or dioxane, in accordance with Reaction scheme 3. In that process it is advantageous to work with a slight excess of trifluoroacetic acid and without an additional solvent at mild temperatures of approx. from 0°C to 25°C or at slightly elevated temperatures of up to approx. 70°C. When trifluoroacetic acid is used as reaction medium, the excess trifluoroacetic acid is subsequently evaporated off *in vacuo*.

The acid of formula Iq is then converted using from 0.50 to approx. 2 equivalents, preferably approx. 1 equivalent, of a water-removing agent, such as phosphorus oxychloride, and a slight excess of from 2.0 to 3.0 equivalents of triethylamine, into the corresponding oxetanone of formula Ir in accordance with Reaction scheme 3 and then reacted with the

corresponding nucleophilic compound of formula V as described for Reaction scheme 2. The novel compounds of formula I_r can either be isolated or, if desired, converted directly into the compounds of formula I_s or, in the case of hydrolysis, into the compounds of formula I_q.

The novel compounds of formula III_a can be prepared analogously to known processes, for example by

a) reacting a hydroxy- or mercapto-pyrimidine or -triazine of formula IV, or a corresponding salt of formula IV_a, which may be prepared *in situ*,



wherein M[⊕] is a cation, such as a sodium, calcium, lithium, magnesium, dimethylammonium or triethylammonium ion, with bromo- or chloro-acetic acid tert-butyl ester in the presence of a base, such as sodium hydrogen carbonate, potassium carbonate, sodium hydride, triethylamine or pyridine, in a suitable solvent, such as acetone, acetonitrile, tetrahydrofuran, ethyl acetate, methyl Cellosolve, dimethoxyethane, toluene, N-methylpyrrolidone, N,N-dimethylformamide, methanol, water or a suitable mixture of the mentioned solvents, in accordance with Reaction scheme 4, Route a); or

b) reacting a corresponding fluoro- or chloro-pyrimidine or -triazine or methyl- or benzylsulfonylpyrimidine of formula VI under the reaction conditions mentioned under a) with hydroxy- or mercapto-acetic acid tert-butyl ester (VIII) in accordance with Reaction scheme 4, Route b).

In particular, compounds of formula III wherein X is sulfur can advantageously be prepared by first converting a compound of formula VI wherein L₄ is methylsulfonyl with sodium hydrogen sulfide into the compound of formula IV_a, which is then reacted *in situ* with bromo- or chloro-acetic acid tert-butyl ester.

For the preparation of compounds of formula III wherein X is oxygen, it has proved advantageous to use bromoacetic acid tert-butyl ester and, where appropriate, to carry out the reaction in the presence of iodide ions. In addition, both in process a) and in process b), the addition of crown ethers can accelerate the reaction.

Compounds of formulae IV, V, VI, VII, VIII and IX wherein R, R₃, R₄, X, Y, Z, A, A_a, L₃, L₄ and L₅ are as defined above are known and can be prepared in accordance with processes known in the literature.

(Per-)haloketones of formula II wherein R₁ and R₂ are as defined above are for the most part known or can be prepared in accordance with known processes, for example analogously to Houben-Weyl 1977, Vol. VII/2c, 2145-2170.

For the use according to the invention of the compounds of formula I, or compositions comprising them, there come into consideration all the methods of application customary in agriculture, such as preemergence application, postemergence application and seed dressing, as well as various methods and techniques, such as the controlled release of active ingredient. For that purpose a solution of the active ingredient is applied to mineral granule carriers or polymerised granules (urea/formaldehyde) and dried. If required, it is also possible to apply a coating (coated granules) which allows the active ingredient to be released in metered amounts over a specific period of time.

The compounds of formula I can be used in unmodified form, i.e. as obtained during synthesis, but are preferably formulated in customary manner together with the adjuvants conventionally employed in formulation technology, e.g. into emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules or microcapsules. As with the nature of the compositions, the methods of application, such as spraying, atomising, dusting, wetting, scattering or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances.

The formulations, i.e. the compositions, preparations or mixtures comprising the compound (active ingredient) of formula I or at least one compound of formula I and, where appropriate, one or more solid or liquid formulation adjuvants, are prepared in known manner, e.g. by homogeneously mixing and/or grinding the active ingredients with the adjuvants, e.g. solvents or solid carriers. Surface-active compounds (surfactants) may

additionally be used in the preparation of the formulations.

Suitable solvents are: aromatic hydrocarbons, preferably the fractions containing 8 to 12 carbon atoms, such as mixtures of alkylbenzenes, e.g. xylene mixtures or alkylated naphthalenes; aliphatic and cycloaliphatic hydrocarbons such as paraffins, cyclohexane or tetrahydronaphthalene; alcohols, such as ethanol, propanol or butanol; glycols and their ethers and esters, such as propylene glycol or dipropylene glycol ether, ketones such as cyclohexanone, isophorone or diacetone alcohol, strongly polar solvents such as N-methyl-2-pyrrolidone, dimethyl sulfoxide or water; vegetable oils and their esters, such as rape oil, castor oil or soybean oil; and optionally also silicone oils.

The solid carriers used e.g. for dusts and dispersible powders are normally natural mineral fillers, such as calcite, talcum, kaolin, montmorillonite or attapulgite. In order to improve the physical properties it is also possible to add highly dispersed silicic acid or highly dispersed absorbent polymers. Suitable granulated adsorptive carriers are porous types, for example pumice, broken brick, sepiolite or bentonite; and suitable non-sorbent carriers are, for example, calcite or sand. In addition, a great number of pregranulated materials of inorganic or organic nature can be used, such as especially dolomite or pulverised plant residues.

Depending on the nature of the compound of formula I to be formulated, suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants having good emulsifying, dispersing and wetting properties. The term "surfactants" will also be understood as comprising mixtures of surfactants.

Both so-called water-soluble soaps and water-soluble synthetic surface-active compounds are suitable anionic surfactants.

Suitable soaps are the alkali metal salts, alkaline earth metal salts or unsubstituted or substituted ammonium salts of higher fatty acids (C₁₀-C₂₂), e.g. the sodium or potassium salts of oleic or stearic acid, or of natural fatty acid mixtures which can be obtained e.g. from coconut oil or tallow oil; mention may also be made of fatty acid methyltaurin salts.

More frequently, however, so-called synthetic surfactants are used, especially fatty alcohol sulfonates, fatty alcohol sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates.

The fatty alcohol sulfonates or sulfates are usually in the form of alkali metal salts, alkaline earth metal salts or unsubstituted or substituted ammonium salts and contain a C₈-C₂₂alkyl radical, which also includes the alkyl moiety of acyl radicals, for example the sodium or calcium salt of lignosulfonic acid, of dodecyl sulfate or of a mixture of fatty alcohol sulfates obtained from natural fatty acids. These compounds also comprise the salts of sulfated and sulfonated fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonic acid groups and one fatty acid radical containing 8 to 22 carbon atoms. Examples of alkylarylsulfonates are the sodium, calcium or triethanolamine salts of dodecylbenzenesulfonic acid, dibutylnaphthalenesulfonic acid or of a condensate of naphthalenesulfonic acid and formaldehyde.

Also suitable are corresponding phosphates, e.g. salts of the phosphoric acid ester of an adduct of p-nonylphenol with 4 to 14 mol of ethylene oxide, or phospholipids.

Non-ionic surfactants are preferably polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, it being possible for said derivatives to contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon moiety and 6 to 18 carbon atoms in the alkyl moiety of the alkylphenols.

Further suitable non-ionic surfactants are water-soluble adducts of polyethylene oxide with polypropylene glycol, ethylenediaminopolypropylene glycol and alkylpolypropylene glycol containing 1 to 10 carbon atoms in the alkyl chain, which adducts contain 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. These compounds usually contain 1 to 5 ethylene glycol units per propylene glycol unit.

Representative examples of non-ionic surfactants are nonylphenol polyethoxyethanols, castor oil polyglycol ethers, polypropylene/polyethylene oxide adducts, tributylphenoxy-polyethoxyethanol, polyethylene glycol and octylphenoxypropylmethoxyethanol.

Fatty acid esters of polyoxyethylene sorbitan, e.g. polyoxyethylene sorbitan trioleate, are also suitable non-ionic surfactants.

Cationic surfactants are preferably quaternary ammonium salts which contain, as N-substituent, at least one C₈-C₂₂alkyl radical and, as further substituents, unsubstituted or

halogenated lower alkyl, benzyl or hydroxy-lower alkyl radicals. The salts are preferably in the form of halides, methyl sulfates or ethyl sulfates, for example stearyltrimethylammonium chloride or benzyl-di(2-chloroethyl)ethylammonium bromide.

The surfactants customarily employed in formulation technology, which can also be used in the compositions according to the invention, are described *inter alia* in the following publications:

- "Mc Cutcheon's Detergents and Emulsifiers Annual", Mc Publishing Corp., Glen Rock, New Jersey, 1988.
- M. and J. Ash, "Encyclopedia of Surfactants", Vol. I-III, Chemical Publishing Co., New York, 1980-1981.
- Dr. Helmut Stache "Tensid-Taschenbuch" (Surfactant Handbook), Carl Hanser-Verlag, Munich/Vienna 1981.

The herbicidal compositions usually comprise 0.1 to 99 %, preferably 0.1 to 95 %, of a compound of formula I, 1 to 99 % of a solid or liquid adjuvant, and 0 to 25 %, preferably 0.1 to 25 %, of a surfactant.

Whereas commercial products are preferably formulated as concentrates, the end user will normally employ dilute formulations.

The compositions may also comprise further ingredients such as stabilisers, e.g. vegetable oils and epoxidised vegetable oils (epoxidised coconut oil, rape oil or soybean oil), anti-foams, e.g. silicone oil, preservatives, viscosity regulators, binders and tackifiers, as well as fertilisers or other active ingredients for obtaining special effects.

Preferred formulations have especially the following composition (throughout, percentages are by weight)

Emulsifiable concentrates:

| | |
|--------------------|---------------------------------|
| active ingredient: | 1 to 90%, preferably 5 to 50% |
| surfactant: | 5 to 30%, preferably 10 to 20% |
| solvent: | 15 to 94%, preferably 70 to 85% |

Dusts:

active ingredient: 0.1 to 50%, preferably 0.1 to 1%
solid carrier: 99.9 to 90%, preferably 99.9 to 99%

Suspension concentrates:

active ingredient: 5 to 75%, preferably 10 to 50%
water: 94 to 24%, preferably 88 to 30%
surfactant: 1 to 40%, preferably 2 to 30%

Wettable powders:

active ingredient: 0.5 to 90%, preferably 1 to 80%
surfactant: 0.5 to 20%, preferably 1 to 15%
solid carrier: 5 to 95%, preferably 15 to 90%

Granules:

active ingredient: 0.1 to 30%, preferably 0.1 to 15%
solid carrier: 99.5 to 70%, preferably 97 to 85%

The compounds of formula I are generally used successfully at rates of application of from 0.001 to 2 kg/ha, especially from 0.005 to 1 kg/ha. The concentration required to achieve the desired effect can be determined by experiment. It is dependent upon the type of action, the stage of development of the crop plant and of the weed, and also upon the application (place, time, method) and, in dependence on those parameters, can vary within wide limits.

The compounds of formula I are distinguished by growth-inhibiting and herbicidal properties that make them outstandingly suitable for use in crops of useful plants, especially in cereals, cotton, soybeans, rape, maize and rice.

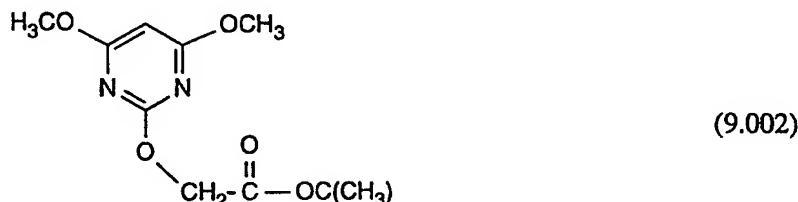
Crops are also to be understood as being those which have been rendered tolerant to herbicides or classes of herbicide by conventional methods of breeding or by genetic techniques.

The Examples that follow further illustrate, but do not limit, the invention.

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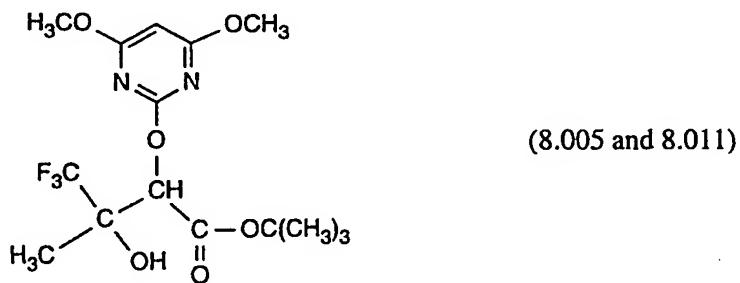
Preparation examples:

Example P1: Preparation of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-acetic acid tert-butyl ester (intermediate)



A mixture of 66.0 g of 4,6-dimethoxy-2-hydroxypyrimidine, 64.0 g of bromoacetic acid tert-butyl ester, 51.0 g of potassium carbonate, 0.5 g of potassium iodide and 0.5 g of 18-crown-6 in 300 ml of dimethylformamide is thoroughly stirred for 80 minutes at 50°C. When the reaction mixture has cooled, it is taken up in diethyl ether and washed 3 times with water and the organic phase is dried over magnesium sulfate. The diethyl ether solution is filtered off and concentrated by evaporation and the residue is dried under a high vacuum. Subsequent distillation in a bulb tube at 125°C/0.2 torr yields the desired product, 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-acetic acid tert-butyl ester; m.p.: 63-64.5°C.

Example P2: Preparation of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-hydroxy-3-trifluoromethylbutyric acid tert-butyl ester



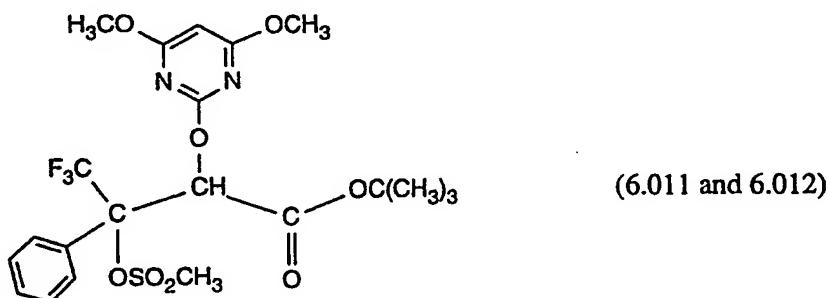
At -78°C (acetone/dry ice bath), 40 ml of a 1.5 molar solution of the lithium diisopropylamide-mono-tetrahydrofuran complex in cyclohexane is placed in a reaction vessel. Then, with thorough stirring, a solution of 15.4 g of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-acetic acid tert-butyl ester (Example P1) in 20 ml of tetrahydrofuran is added. After

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45 minutes, at a temperature below -70°C 7.5 ml of trifluoroacetone are added dropwise and the reaction mixture is then stirred for 10 minutes at -70°C and for 10 minutes at -50°C and then allowed to warm to 0°C. 100 ml of 5 % aqueous ammonium chloride solution are added to that reaction mixture which is then extracted by shaking with diethyl ether. The organic phase is separated off, washed with dilute hydrochloric acid solution and sodium chloride solution and then concentrated by evaporation. By means of crystallisation from ethyl acetate/hexane 1/30, isomer I can be obtained in the form of white crystals having a melting point of 135-137°C. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 5.77 ppm (s, 1H), 5.30 ppm (s, 1H), 3.95 ppm (s, 6H), 3.72 ppm (s, 1H), 1.62 ppm (s, 3H), 1.41 ppm (s, 9H). From the mother liquor consisting of an approx. 1:7 mixture of isomer I and isomer II there is obtained by means of column chromatography (eluant diethyl ether/hexane = 1/4) the pure isomer II of the desired 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-hydroxy-3-trifluoromethylbutyric acid tert-butyl ester having a melting point of 69-70°C.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): 5.77 ppm (s, 1H), 5.22 ppm (s, 1H), 3.95 ppm (s, 6H), 3.68 ppm (s, 1H), 1.54 ppm (s, 3H), 1.40 ppm (s, 9H).

Example P3: Preparation of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-mesyloxy-3-phenyl-3-trifluoromethyl-propionic acid tert-butyl ester



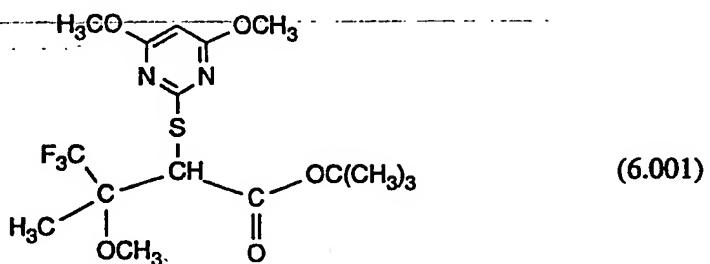
7.0 g of the isomeric mixture of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-hydroxy-3-phenyl-3-trifluoromethyl-propionic acid tert-butyl ester (Comp. No. 8.006) are heated at reflux temperature in the presence of 6.4 g of triethylamine and 0.24 g of diazabicyclo-undecene (DBU) with 3.6 g of methanesulfonic acid chloride in 20 ml of toluene. After 5 hours, the reaction mixture is washed once each with aqueous sodium hydrogen carbonate solution, dilute hydrochloric acid and saturated sodium chloride solution and concentrated by evaporation using a Rotovap. The resulting crude product is separated by chromatography on silica gel (eluant diethyl ether/hexane 3/7). There is obtained as first

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fraction isomer I of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-mesyloxy-3-phenyl-3-trifluoromethyl-propionic acid tert-butyl ester: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.94 ppm (m, 2H), 7.45 ppm (m, 3H), 6.81 ppm (s, 1H), 5.78 ppm (s, 1H), 3.93 ppm (s, 6H), 3.40 ppm (s, 3H), 1.18 ppm (s, 9H).

There is obtained as second fraction isomer II of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-mesyloxy-3-phenyl-3-trifluoromethyl-propionic acid tert-butyl ester: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.75 ppm (m, 2H), 7.47 ppm (m, 3H), 6.20 ppm (s, 1H), 5.78 ppm (s, 1H), 3.91 ppm (s, 6H), 3.34 ppm (s, 3H), 1.28 ppm (s, 9H).

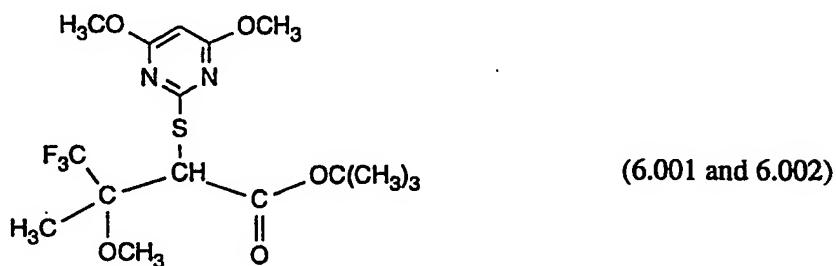
Example P4: Preparation of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3-trifluoromethyl-butyric acid tert-butyl ester



3.0 g of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-hydroxy-3-trifluoromethyl-butyric acid tert-butyl ester (Comp. No. 8.001) are added at 0°C to 0.32 g of a 60 % dispersion of sodium hydride in oil and the mixture is then stirred for 5 minutes at 25°C; 1.32 ml of methyl iodide are added thereto and the reaction mixture is heated slowly to 40°C. The reaction mixture is then extracted with ethyl acetate and the organic phases are combined, washed with dilute hydrochloric acid and saturated sodium chloride solution, dried over magnesium sulfate and concentrated by evaporation using a Rotovap. The residue that remains is filtered over silica gel. There is obtained as pure isomer I 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3-trifluoromethyl-butyric acid tert-butyl ester: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 5.78 ppm (s, 1H), 5.24 ppm (s, 1H), 3.94 ppm (s, 6H), 3.50 ppm (s, 3H), 1.45 ppm (s, 9H).

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Example P5: Preparation of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3-trifluoromethyl-butyric acid tert-butyl ester (*in situ* method)

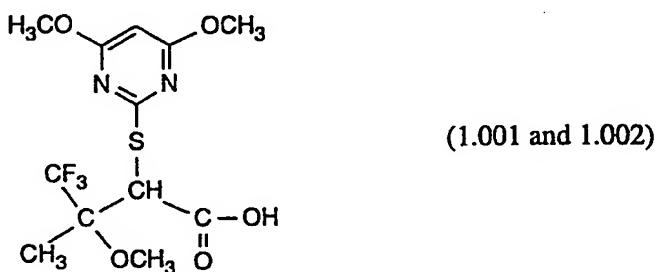


26.0 g of 2-[4,6-dimethoxy-pyrimidin-2-yl]-thio]-acetic acid tert-butyl ester (Comp. No. 9.001, Example P7) are added in 40 ml of absolute tetrahydrofuran at a temperature below -73°C to a prepared solution of 16.7 g of lithium bis(trimethylsilyl)amide in 100 ml of hexane and 40 ml of absolute tetrahydrofuran. When the addition is complete, the reaction mixture is stirred for 20 minutes and then, at a temperature below -70°C, 11.5 ml of 1,1,1-trifluoromethylacetone are added. The temperature of the reaction mixture is allowed to rise slowly to room temperature and then 8.7 ml of dimethyl sulfate are added. That reaction mixture is then heated at the reflux temperature for 3 hours (internal temperature of reaction vessel 60°C). The reaction mixture is cooled, taken up in diethyl ether, washed in succession with water, sodium hydrogen carbonate solution, dilute hydrochloric acid and saturated sodium chloride solution, dried over magnesium sulfate and concentrated by evaporation *in vacuo*. The residue that remains is purified on silica gel with 5-10 % diethyl ether in hexane as eluant. There is obtained as first fraction 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3-trifluoromethyl-butyric acid tert-butyl ester in the form of an isomeric mixture in a ratio of 84/16. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 5.78 and 5.76 ppm (2s, 1H), 5.24 and 5.16 ppm (2s, 1H), 3.94 ppm (s, 6H), 3.50 and 3.45 ppm (2s, 3H), 1.71 and 1.62 ppm (2s, 3H), 1.45 and 1.43 ppm (2s, 9H).

Further elution with 10-20% diethyl ether in hexane yields as further extracts the isomers of 2-[4,6-dimethoxy-pyrimidin-2-yl]-thio]-3-hydroxy-3-trifluoromethyl-butyric acid tert-butyl ester (Comp. No. 8.001 and 8.002); $^1\text{H-NMR}$ (300 MHz, CDCl_3): isomer I: 5.80 ppm (s, 1H), 5.23 ppm (s, 1H), 5.04 ppm (s, 1H), 3.95 ppm (s, 6H), 1.48 ppm (s, 12H); isomer II: 5.84 ppm (s, 1H), 5.66 ppm (s, 1H), 4.71 ppm (s, 1H), 3.95 ppm (s, 6H), 1.58 ppm (s, 3H), 1.46 ppm (s, 9H).

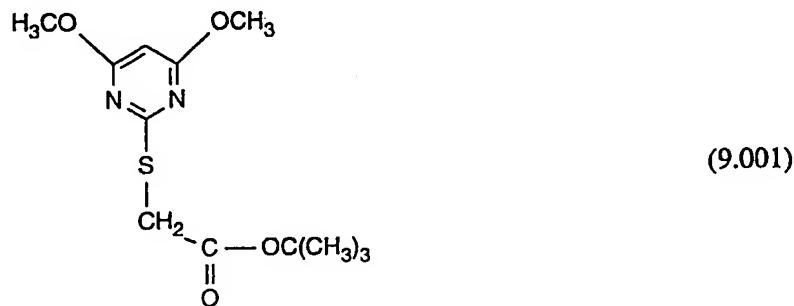
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Example P6: Preparation of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3-trifluoromethyl-butyric acid



12.1 g of an isomeric mixture of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3-trifluoromethyl-butyric acid tert-butyl ester (Example P5) are left to stand for 3 hours in 20 ml of trifluoroacetic acid at room temperature. The reaction mixture is then concentrated by evaporation *in vacuo* and, for purification, taken up in diethyl ether and extracted with ice-cold sodium hydroxide solution. The aqueous phase is adjusted to pH 3 and the product is extracted with ethyl acetate. The organic phase is washed with saturated sodium chloride solution and then dried over sodium sulfate and concentrated by evaporation *in vacuo*. There is obtained by means of crystallisation from chloroform/hexane 1/5, in the form of white crystals, an 88/12 isomeric mixture of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3-trifluoromethyl-butyric acid having a melting point of 124.5-125.5°C; ¹H-NMR (300 MHz, CDCl₃): isomer I: 5.81 ppm (s, 1H), 5.22 ppm (s, 1H), 3.94 ppm (s, 6H), 3.52 ppm (s, 3H), 1.73 ppm (s, 3H); isomer II: 5.78 ppm (s, 1H), 5.08 ppm (s, 1H), 3.92 ppm (s, 6H), 3.48 ppm (s, 3H), 1.66 ppm (s, 3H).

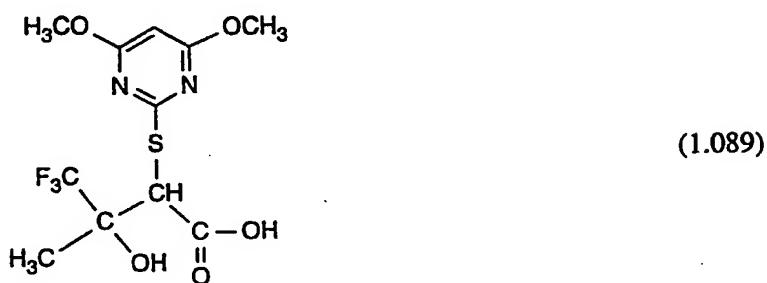
Example P7: Preparation of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-acetic acid tert-butyl ester (intermediate)



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58.5 g of 95 % sodium hydrogen sulfide-monohydrate and 76.4 g of 4,6-dimethoxy-pyrimidine-2-methylsulfone in a mixture of 350 ml of tetrahydrofuran and 500 ml of methanol are heated with vigorous stirring for 25 minutes at 60°C. The reaction mixture is then cooled to room temperature and 78.0 g of bromoacetic acid tert-butyl ester are added dropwise thereto. After brief heating at 45°C, most of the solvent is distilled off and the residue is taken up in diethyl ether. The organic phase is washed with dilute sodium hydroxide solution and then with sodium chloride solution and evaporated. Vacuum distillation at 130°C/1x10⁻² torr yields the desired product, 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-acetic acid tert-butyl ester, in the form of a slightly yellowish liquid which changes to a wax-like state when left to stand.

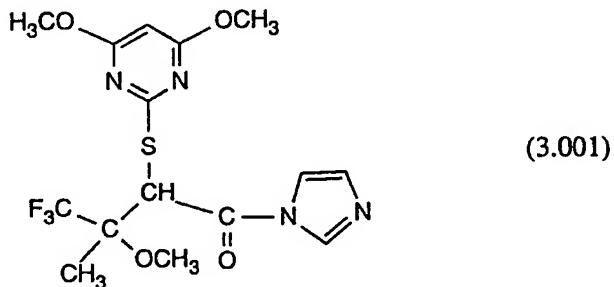
Example P8: Preparation of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-hydroxy-3-trifluoromethylbutyric acid



1.2 g of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-hydroxy-3-trifluoromethylbutyric acid tert-butyl ester (Compound No. 8.002) are left to stand for 2 hours in 3 ml of trifluoroacetic acid at room temperature. The reaction mixture is then concentrated by evaporation *in vacuo*, the residue is dissolved in diethyl ether and extraction is carried out with dilute sodium hydroxide solution. The alkaline/aqueous phase is separated off, adjusted to pH 2.5 and extracted again with diethyl ether. The organic phase is concentrated by evaporation and the desired product, 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-hydroxy-3-trifluoromethylbutyric acid, is obtained in the form of crystals; m.p.: 123-124°C.

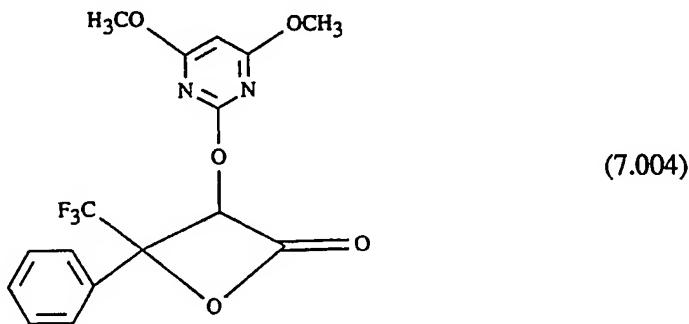
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Example P9: Preparation of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3-trifluoromethyl-butyric acid imidazolide



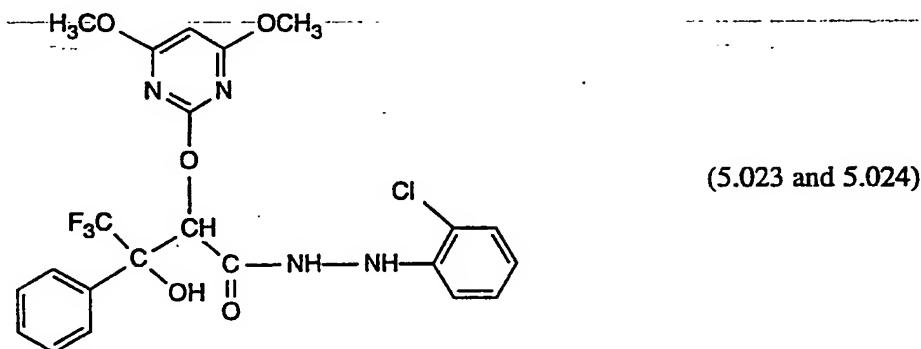
3.75 g of 1,1-carbonyldiimidazole are placed in 22 ml of dichloromethane. At a temperature below 5°C, 6.53 g of the isomeric mixture of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3-trifluoromethyl-butyric acid (Example P6) dissolved in 12 ml of dimethylformamide are added dropwise thereto. The mixture is heated to room temperature and then stirred for 1 hour and the resulting reaction mixture is extracted with dichloromethane, washed with ice-cold 5 % sodium chloride solution, dried over magnesium sulfate and concentrated by evaporation *in vacuo*. The resulting oily product is the isomeric mixture of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3-trifluoromethyl-butyric acid imidazolide; $^1\text{H-NMR}$ (300 MHz, CDCl_3): 8.42 and 8.35 ppm (1H), 7.64 and 7.61 ppm (1H), 7.10 and 7.08 ppm (1H), 5.92 and 5.85 ppm (2s, 1H), 5.81 and 5.80 ppm (2s, 1H), 3.90 and 3.86 ppm (2s, 6H), 3.48 and 3.38 ppm (2s, 3H), 1.84 and 1.75 ppm (2s, 3H).

Example P10: Preparation of the isomers of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxyl]-3-phenyl-3-trifluoromethyl-propiolactone



3.0 g of the isomeric mixture of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-hydroxy-3-phenyl-3-trifluoromethyl-propionic acid (Compound Nos. 1.092 and 1.093) are dissolved in 30 ml of dichloromethane and at -10°C first 2.7 ml of triethylamine and then 0.38 ml of phosphorus oxychloride are added and the mixture is stirred for 10 minutes at -5°C. The resulting reaction mixture is washed twice with a small amount of ice-cold water and the organic phase is separated off, dried and concentrated by evaporation. The resulting amorphous residue is an isomeric mixture of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-phenyl-3-trifluoromethylpropiolactone; m.p. 100-106°C.

Example P11: Preparation of the isomers of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-hydroxy-3-phenyl-3-trifluoromethyl-propionic acid 2-chlorophenyl hydrazide



1.5 g of the propiolactone from Example P10 are again dissolved in 10 ml of dichloromethane and at 20°C first 0.37 g of ortho-chlorophenylhydrazine-hydrochloride and then 0.57 ml of triethylamine are added thereto and the mixture is stirred for 30 minutes. Diethyl ether is added to the resulting reaction mixture which is then extracted twice with sodium carbonate solution to regenerate 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-hydroxy-3-phenyl-3-trifluoromethyl-propionic acid (Compound Nos. 1.092 and 1.093). The organic phase is then separated off, washed with dilute hydrochloric acid and then with aqueous sodium chloride solution, dried and concentrated by evaporation. The resulting residue is separated by column chromatography (eluant hexane/diethyl ether = 3/2) into the two isomers of 2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-hydroxy-3-phenyl-3-trifluoromethylpropionic acid 2-chlorophenyl hydrazide. isomer I: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 8.21 ppm (d, 1H), 7.96 ppm (broad signal, 2H), 7.50 ppm (broad signal, 3H), 7.18 ppm (m, 1H), 6.75 ppm (m, 2H), 6.52 ppm (s, 1H), 6.08 ppm (d, 1H), 5.90 ppm (s, 1H), 5.88 ppm (s, 1H), 5.00 ppm (m, 1H), 3.99 ppm

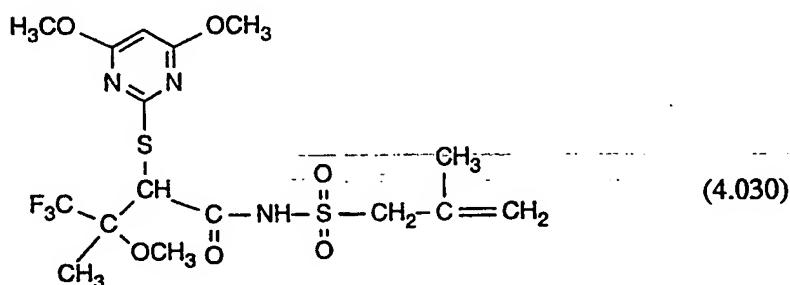
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(s, 6H).

isomer II: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 8.20 ppm (d, 1H), 7.71 ppm (broad signal, 2H), 7.36 ppm (broad signal, 3H), 7.19 ppm (d, 1H), 6.96 ppm (t, 1H), 6.78 ppm (t, 1H), 6.26 ppm (d, 1H), 6.22 ppm (d, 1H), 6.12 ppm (s, 1H), 5.76 ppm (s, 1H), 5.32 ppm (s, 1H), 3.85 ppm (s, 6H).

Example P12: Preparation of 2-[4,6-dimethoxy-pyrimidin-2-yl]-thio]-3-methoxy-3-trifluoromethylbutyric acid 2-methyl-2-propenylsulfonamide



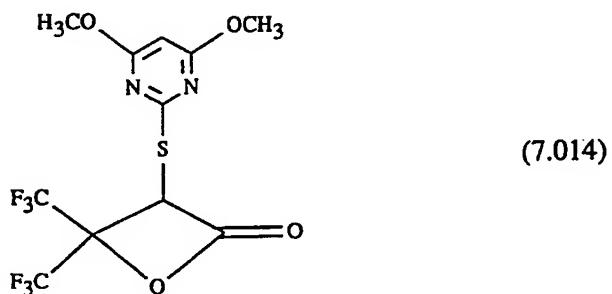
0.54 g of methyl-2-propenylsulfonamide is added at 0-5°C to a suspension of 0.17 g of sodium hydride, in the form of a 60 % dispersion in oil, and the reaction mixture is then stirred at room temperature until the evolution of hydrogen is complete. After 30 minutes, at 0-5°C 1.63 g of 2-[4,6-dimethoxy-pyrimidin-2-yl]-thio]-3-methoxy-3-trifluoromethylbutyric acid imidazolide (Example P9) dissolved in 5 ml of N,N-dimethylformamide are added dropwise. Stirring is then continued for 4 hours at room temperature and the reaction mixture is then extracted with ethyl acetate. The combined organic phases are washed in succession with water, dilute hydrochloric acid and sodium chloride solution, dried over magnesium sulfate and concentrated by evaporation *in vacuo*. Purification by column chromatography (eluant 15 % acetone/hexane) yields the concentrated isomers of 2-[4,6-dimethoxy-pyrimidin-2-yl]-thio]-3-methoxy-3-trifluoromethylbutyric acid 2-methyl-2-propenylsulfonamide.

isomer I: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 8.98 ppm (broad signal, 1H), 5.73 ppm (s, 1H), 5.14 and 5.08 ppm (2xs, 2H), 4.95 ppm (s, 1H), 4.05 ppm (broad signal, 2H), 3.94 ppm (s, 6H), 3.54 ppm (s, 3H), 1.94 ppm (s, 3H), 1.72 ppm (s, 3H);

isomer II: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 9.00 ppm (broad signal), 5.71 ppm (s, 1H), 5.02 and 4.96 ppm (2xd, 2H), 4.70 ppm (s, 1H), 4.10 ppm (broad signal, 2H), 3.94 ppm (s, 6H), 1.85 ppm (s, 3H), 1.68 ppm (s, 3H).

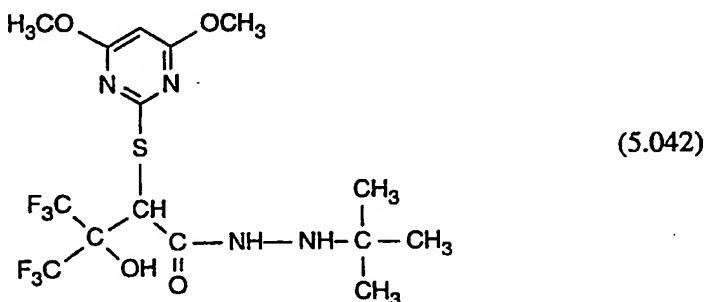
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Example P13: Preparation of 2-[(4,6-dimethoxypyrimidin-2-yl)-thio]-3,3-bis-trifluoromethyl-propiolactone (Compound No. 7.014)



3.5 g of 2-[(4,6-dimethoxypyrimidin-2-yl)-thio]-3,3-bis-trifluoromethylbutyric acid (Compound No. 1.094) are placed at 0°C in 20 ml of dichloromethane and treated in the presence of 0.12 ml of triethylamine with 1.9 g of N,N-dicyclohexylcarbodiimide. The reaction mixture is then stirred for approx. 30 minutes at 22°C and the N,N'-dicyclohexylurea that has precipitated is filtered off. The filtrate is concentrated to dryness by evaporation. The crude desired product is obtained; $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.10 ppm (s, 1H), 5.88 ppm (s, 1H), 3.92 ppm (s, 6H).

Example P14: Preparation of 2-[(4,6-dimethoxypyrimidin-2-yl)-thio]-3-hydroxy-3,3-bis-trifluoromethylbutyric acid tert-butyl hydrazide (Compound No. 5.042)



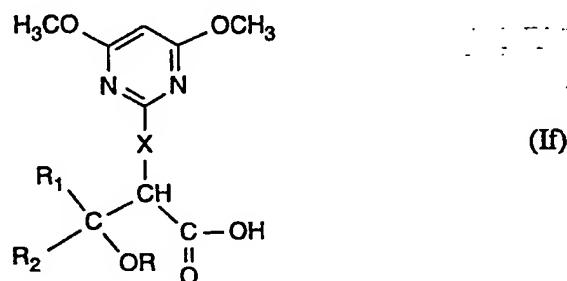
3.0 g of the 2-[(4,6-dimethoxypyrimidin-2-yl)-thio]-3,3-bis-trifluoromethyl-propiolactone (Compound No. 7.014) prepared in Example P13 are dissolved in tetrahydrofuran and the solution is treated in succession at 0°C with 1.0 g of tert-butyl hydrazide hydrochloride and 1.14 ml of triethylamine. After stirring for one hour at 22°C, the reaction mixture is diluted with diethyl ether and washed in succession with 1N hydrochloric acid, 5 %

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sodium hydrogen carbonate solution and 30 % sodium chloride solution. The residue is concentrated to dryness by evaporation and purified by chromatography on silica gel with ethyl acetate/hexane 1/9 to 1/3 as eluant. The desired compound is obtained as an amorphous product. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 8.55 ppm (broad signal, NH), 8.16 ppm (broad signal, OH), 5.86 ppm (s, 1H), 5.25 ppm (s, 1H), 4.63 ppm (broad signal, NH), 3.92 ppm (s, 6H), 1.03 ppm (s, 9H).

The compounds listed in Tables 1 to 8 and the intermediates of Table 9 can be prepared in analogous manner.

Table 1: Compounds of formula If



| Comp. No. | X | R_1 | R_2 | R | Phys. data |
|--------------|---|---------------|------------------------|--------------------------|------------------------------|
| 1.001 | S | CF_3 | CH_3 | CH_3 | isomer I: Example P6 |
| 1.002 | S | CF_3 | CH_3 | CH_3 | isomer II: m.p. 126-128°C |
| 1.003 | S | CF_3 | phenyl | CH_3 | isomer I: m.p. 136-138°C |
| 1.004 | S | CF_3 | phenyl | CH_2CH_3 | |
| 1.005 | O | CF_3 | phenyl | CH_3 | |
| 1.006 | O | CF_3 | phenyl | CH_2CH_3 | |
| 1.007 | O | CF_3 | CF_3 | CH_3 | |
| 1.008 | S | CF_3 | CF_3 | CH_3 | m.p. 146-147°C |
| 1.009 | O | CF_3 | CF_2Cl | CH_3 | |
| 1.010 | S | CF_3 | CF_2Cl | CH_3 | |
| 1.011 | O | CF_3 | CCl_3 | CH_3 | |

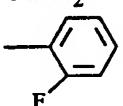
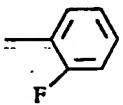
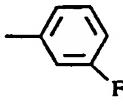
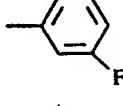
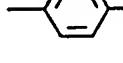
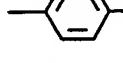
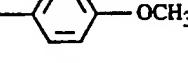
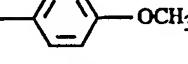
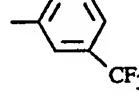
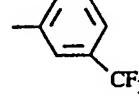
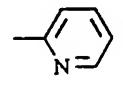
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| Comp. No. | X | R ₁ | R ₂ | R | Phys. data |
|-----------|---|----------------|----------------|---|------------|
|-----------|---|----------------|----------------|---|------------|

| | | | | | |
|-------|---|---|---------------------------------|-----------------|--|
| 1.012 | S | CF ₃ | CCl ₃ | CH ₃ | |
| 1.013 | O | CF ₂ Cl | CF ₂ Cl | CH ₃ | |
| 1.014 | S | CF ₂ Cl | CF ₂ Cl | CH ₃ | |
| 1.015 | O | CF ₂ Cl | CFCl ₂ | CH ₃ | |
| 1.016 | S | CF ₂ Cl | CFCl ₂ | CH ₃ | |
| 1.017 | O | CF ₂ Cl | phenyl | CH ₃ | |
| 1.018 | S | CF ₂ Cl | phenyl | CH ₃ | |
| 1.019 | O | CF ₂ CF ₃ | phenyl | CH ₃ | |
| 1.020 | S | CF ₂ CF ₃ | phenyl | CH ₃ | |
| 1.021 | O | CF ₂ CF ₃ | CH ₃ | CH ₃ | |
| 1.022 | S | CF ₂ CF ₃ | CH ₃ | CH ₃ | |
| 1.023 | O | CF ₂ CF ₃ | CF ₂ CF ₃ | CH ₃ | |
| 1.024 | S | CF ₂ CF ₃ | CF ₂ CF ₃ | CH ₃ | |
| 1.025 | O | CF ₂ CF ₂ CF ₃ | phenyl | CH ₃ | |
| 1.026 | S | CF ₂ CF ₂ CF ₃ | phenyl | CH ₃ | |
| 1.027 | O | CF ₂ CF ₂ CF ₃ | CH ₃ | CH ₃ | |
| 1.028 | S | CF ₂ CF ₂ CF ₃ | CH ₃ | CH ₃ | |
| 1.029 | O | CCl ₃ | phenyl | CH ₃ | |
| 1.030 | S | CCl ₃ | phenyl | CH ₃ | |
| 1.031 | O | CCl ₃ | CFCl ₂ | CH ₃ | |
| 1.032 | S | CCl ₃ | CFCl ₂ | CH ₃ | |
| 1.033 | O | CCl ₃ | CHCl ₂ | CH ₃ | |
| 1.034 | S | CCl ₃ | CHCl ₂ | CH ₃ | |
| 1.035 | O | CCl ₃ | H | CH ₃ | |
| 1.036 | S | CCl ₃ | H | CH ₃ | |
| 1.037 | O | CBr ₃ | H | CH ₃ | |
| 1.038 | S | CBr ₃ | H | CH ₃ | |
| 1.039 | O | CF ₂ Cl | H | CH ₃ | |
| 1.040 | S | CF ₂ Cl | H | CH ₃ | |
| 1.041 | O | CF ₂ CF ₃ | H | CH ₃ | |
| 1.042 | S | CF ₂ CF ₃ | H | CH ₃ | |
| 1.043 | O | CF ₂ CF ₂ CF ₃ | H | CH ₃ | |

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| Comp. No. | X | R ₁ | R ₂ | R | Phys. data |
|--------------|---|----------------|----------------|---|------------|
|--------------|---|----------------|----------------|---|------------|

| | | | | | |
|-------|---|---|---|-----------------|--|
| 1.044 | S | CF ₂ CF ₂ CF ₃ | H | CH ₃ | |
| 1.045 | O | CF ₃ | CHBr ₂ | CH ₃ | |
| 1.046 | S | CF ₃ | CHBr ₂ | CH ₃ | |
| 1.047 | O | CF ₂ CF ₃ | CHBr ₂ | CH ₃ | |
| 1.048 | S | CF ₂ CF ₃ | CHBr ₂ | CH ₃ | |
| 1.049 | O | CF ₃ |  | CH ₃ | |
| 1.050 | S | CF ₃ |  | CH ₃ | |
| 1.051 | O | CF ₃ |  | CH ₃ | |
| 1.052 | S | CF ₃ |  | CH ₃ | |
| 1.053 | O | CF ₃ |  | CH ₃ | |
| 1.054 | S | CF ₃ |  | CH ₃ | |
| 1.055 | O | CF ₃ |  | CH ₃ | |
| 1.056 | S | CF ₃ |  | CH ₃ | |
| 1.057 | O | CF ₃ |  | CH ₃ | |
| 1.058 | S | CF ₃ |  | CH ₃ | |
| 1.059 | O | CF ₃ |  | CH ₃ | |

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| Comp. No. | X | R ₁ | R ₂ | R | Phys. data |
|--------------|---|-----------------|---------------------------------|------------------------------------|---|
| 1.060 | S | CF ₃ | | CH ₃ | |
| 1.061 | O | CF ₃ | | CH ₃ | |
| 1.062 | S | CF ₃ | | CH ₃ | |
| 1.063 | O | CF ₃ | | CH ₃ | |
| 1.064 | S | CF ₃ | | CH ₃ | |
| 1.065 | O | CF ₃ | CH ₃ | CH ₂ CH ₃ | isomer I: m.p. 99-101°C |
| 1.066 | S | CF ₃ | CH ₃ | CH ₂ CH ₃ | isomer I: m.p. 138.9-139.3°C |
| 1.067 | S | CF ₃ | CH ₃ | CH ₂ CH ₃ | isomer II: ¹ H-NMR (300 MHz, CDCl ₃): 5.78 ppm (s, 1H), 5.09 ppm (s, 1H), 3.90 ppm (s, 6H), 3.72 ppm (q, 2H), 1.66 ppm (s, 3H), 1.17 ppm (t, 3H). |
| 1.068 | O | CF ₃ | CH ₂ CH ₃ | CH ₃ | |
| 1.069 | S | CF ₃ | CH ₂ CH ₃ | CH ₃ | |
| 1.070 | O | CF ₃ | CH ₂ CH ₃ | CH ₂ CH ₃ | |
| 1.071 | S | CF ₃ | CH ₂ CH ₃ | CH ₂ CH ₃ | |
| 1.072 | O | CF ₃ | CH ₃ | CH ₂ CH=CH ₂ | 4:1 isomeric mixture: m.p. 63-67°C |
| 1.073 | S | CF ₃ | CH ₃ | CH ₂ CH=CH ₂ | |
| 1.074 | O | CF ₃ | CH ₃ | CH ₂ C≡CH | |
| 1.075 | S | CF ₃ | CH ₃ | CH ₂ C≡CH | |

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| Comp. No. | X | R ₁ | R ₂ | R | Phys. data |
|--------------|---|-----------------|--------------------|--|--|
| 1.076 | O | CF ₃ | CH ₃ | CH ₂ CH ₂ Cl | |
| 1.077 | S | CF ₃ | CH ₃ | CH ₂ CH ₂ Cl | |
| 1.078 | O | CF ₃ | CH ₃ | CH ₂ CH ₂ F | |
| 1.079 | S | CF ₃ | CH ₃ | CH ₂ CH ₂ F | |
| 1.080 | O | CF ₃ | CH ₃ | CH ₂ CH ₂ OCH ₃ | |
| 1.081 | S | CF ₃ | CH ₃ | CH ₂ CH ₂ OCH ₃ | |
| 1.082 | O | CF ₃ | CH ₃ | CH ₂ CH ₂ OCH ₂ CH ₃ | |
| 1.083 | S | CF ₃ | CH ₃ | CH ₂ CH ₂ OCH ₂ CH ₃ | |
| 1.084 | O | CF ₃ | CH ₃ | CH ₂ CH ₂ C≡CH | |
| 1.085 | S | CF ₃ | CH ₃ | CH ₂ CH ₂ C≡CH | |
| 1.086 | O | CF ₃ | CH ₃ | benzyl | 3:1 isomeric mixture; m.p. 134-136°C |
| 1.087 | S | CF ₃ | CH ₃ | benzyl | |
| 1.088 | S | CF ₃ | CH ₃ | H | isomer I: m.p. 118-119°C |
| 1.089 | S | CF ₃ | CH ₃ | H | isomer II: m.p. 123-124°C (Example P8) |
| 1.090 | S | CF ₃ | phenyl | H | isomer I: m.p. 172-173°C |
| 1.091 | S | CF ₃ | phenyl | H | isomer II: m.p. 150-151°C |
| 1.092 | O | CF ₃ | phenyl | H | isomer I: m.p. 159-160°C |
| 1.093 | O | CF ₃ | phenyl | H | isomer II: ¹ H-NMR (300 MHz, CDCl ₃): 7.68 ppm (broad signal, 2H), 7.42 ppm (broad signal, 3H), 5.78 ppm (s, 1H), 5.76 ppm (s, 1H), 3.85 ppm (s, 3H); m.p. 160°C. |
| 1.094 | S | CF ₃ | CF ₃ | H | m.p. 173-174°C |
| 1.095 | S | CF ₃ | CF ₂ Cl | H | |

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| Comp. No. | X | R ₁ | R ₂ | R | Phys. data |
|--------------|---|---|--------------------|---|--|
| 1.096 | S | CF ₃ | CCl ₃ | H | |
| 1.097 | S | CF ₂ Cl | CF ₂ Cl | H | |
| 1.098 | S | CF ₂ Cl | CFCl ₂ | H | |
| 1.099 | S | CF ₂ CF ₃ | CH ₃ | H | |
| 1.100 | S | CF ₂ CF ₂ CF ₃ | CH ₃ | H | |
| 1.101 | S | CCl ₃ | CFCl ₂ | H | |
| 1.102 | S | CCl ₃ | CHCl ₂ | H | |
| 1.103 | S | CCl ₃ | H | H | |
| 1.104 | S | CBr ₃ | H | H | |
| 1.105 | S | CF ₂ Cl | H | H | |
| 1.106 | S | CF ₂ CF ₃ | H | H | |
| 1.107 | S | CF ₂ CF ₂ CF ₃ | H | H | |
| 1.108 | S | CF ₃ | CHBr ₂ | H | |
| 1.109 | S | CF ₂ CF ₃ | CHBr ₂ | H | |
| 1.110 | O | CF ₃ | CH ₃ | H | isomer I: ¹ H-NMR (300 MHz, D ₆ -DMSO): 13.15 ppm (broad signal, 1H), 6.75 ppm (broad signal, 1H); 5.94 ppm (s, 1H), 5.16 ppm (s, 1H), 3.86 ppm (s, 3H), 1.50 ppm (s, 3H); m.p. 167-168°C. |
| 1.111 | O | CF ₃ | CH ₃ | H | isomer II: ¹ H-NMR (300 MHz, D ₆ -DMSO): 13.25 ppm (broad signal, 1H), 6.65 ppm (s, 1H), 5.94 ppm (s, 1H), 5.06 ppm (s, 1H), 3.86 ppm (s, 3H), 1.50 ppm (s, 3H); m.p. 146-147°C. |
| 1.112 | S | CH ₃ | CH ₃ | H | m.p. 124-126°C |

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| Comp. No. | X | R ₁ | R ₂ | R | Phys. data |
|--------------|---|-------------------------------|------------------------------------|-------------------------------|---|
| 1.113 | S | | -(CH ₂) ₄ - | H | m.p. 123.7-124.3°C |
| 1.114 | S | CH ₃ | | C ₂ H ₅ | ¹ H-NMR (300 MHz, CDCl ₃): 5.82 ppm (s, 1H), 4.45 ppm (s, 1H), 3.95 ppm (s, 6H), 1.84 ppm (m, 2H), 1.45 ppm (s, 3H), 0.95 ppm (s, 3H); m.p. 132-133°C; isomer I |
| 1.115 | S | C ₂ H ₅ | | CH ₃ | ¹ H-NMR (300 MHz, CDCl ₃): 5.82 ppm (s, 1H), 4.47 ppm (s, 1H), 3.95 ppm (s, 6H), 1.82 ppm (q, 2H), 1.41 ppm (s, 3H), 1.00 ppm (t, 3H); isomer II. |
| 1.116 | O | CH ₃ | | CH ₃ | ¹ H-NMR (300 MHz, CDCl ₃): 6.75 ppm (broad signal, 1H), 5.75 ppm (s, 1H), 5.00 ppm (s, 1H), 3.88 ppm (s, 6H), 1.03 and 1.05 ppm (2xs, 6H). |
| 1.117 | S | CF ₃ | | CF ₃ | H m.p. 202-204°C; imidazolium salt of Comp. No. 1.094 |
| 1.118 | O | CH ₃ | | C ₂ H ₅ | H ¹ H-NMR (300 MHz, CDCl ₃): 6.20 ppm (broad signal, 1H), 5.75 ppm (s, 1H), 5.10 ppm (s, 1H), |

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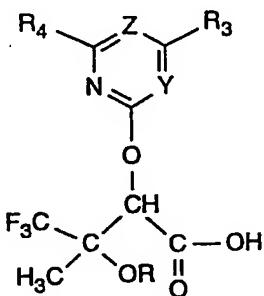
| Comp. No. | X | R ₁ | R ₂ | R | Phys. data |
|--------------|---|-------------------------------|-----------------|---------------------------------|---|
| 1.119 | O | C ₂ H ₅ | CH ₃ | H | 3.89 ppm (s, 6H), 1.78 ppm (dxq, 2H), 1.40 ppm (s, 3H), 1.00 ppm (t, 3H); m.p. 117-118°C; isomer I ¹ H-NMR (300 MHz, CDCl ₃): 6.60 ppm (broad signal, 1H), 5.78 ppm (s, 1H), 5.05 ppm (s, 1H), 3.89 ppm (s, 6H), 1.30 ppm (m, 2H), 1.38 ppm (s, 3H), 0.98 ppm (t, 3H); isomer II. |
| 1.120 | O | CF ₃ | CH ₃ | CH ₂ CH ₃ | isomer II: m.p. 116-117°C |
| 1.121 | S | CF ₃ | phenyl | CH ₃ | isomeric mixture: m.p. 133-136°C |
| 1.122 | S | CF ₃ | phenyl | CH ₃ | isomer II: ¹ H-NMR (300 MHz, CDCl ₃): 7.52 ppm (2H), 7.46 ppm (3H), 5.74 ppm (s, 1H), 5.27 ppm (s, 1H), 3.88 ppm (s, 6H), 3.54 ppm (s, 3H). |
| 1.123 | S | CF ₃ | CH ₃ | CH ₂ CH ₃ | isomeric mixture: m.p. 119-121°C |
| 1.124 | S | CH ₃ | phenyl | H | isomer I: m.p. 146°C; ¹ H-NMR (300 MHz, CDCl ₃): 5.87 ppm (s, 1H), 4.94 ppm (s, 1H), 3.98 ppm (s, 6H), |

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| Comp. No. | X | R ₁ | R ₂ | R | Phys. data |
|--------------|---|--|-----------------|---------------------------------|--|
| 1.125 | S | CH ₃ | phenyl | H | 1.70 ppm (s, 3H). isomer II: m.p. 145°C; ¹ H-NMR (300 MHz, CDCl ₃): 5.77 ppm (s, 1H), 4.62 ppm (s, 1H), 3.92 ppm (s, 6H), 1.83 ppm (s, 3H). |
| 1.126 | S | CF ₃ | CH ₃ | SO ₂ CH ₃ | isomer II: ¹ H-NMR (300 MHz, CDCl ₃): 8.35 ppm (broad signal, 1H), 5.80 ppm (s, 1H), 5.78 ppm (s, 1H), 3.92 ppm (s, 6H), 2.86 ppm (s, 3H), 2.18 ppm (s, 3H). |
| 1.127 | S | -CH ₂ CH ₂ CH ₂ CH ₂ - | | H | m.p. 124-125°C |

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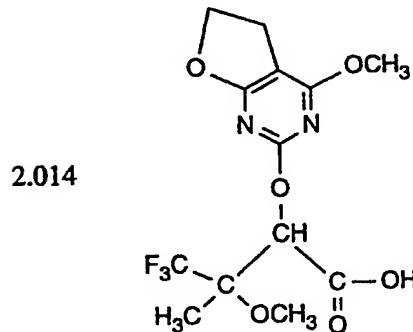
Table 2: Compounds of formula Ig



(Ig)

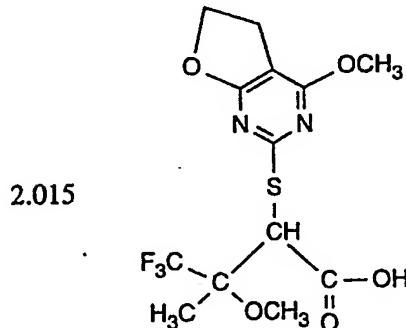
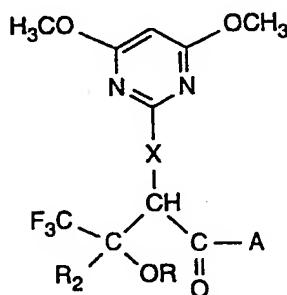
| Comp. No. | Y | Z | R ₃ | R ₄ | R | Phys. data |
|-----------|---|---|----------------|----------------|---|------------|
|-----------|---|---|----------------|----------------|---|------------|

| | | | | | | |
|-------|----|----|--------------------------------|----------------------------------|-----------------|---------------------------|
| 2.001 | N | CH | OCH ₃ | OCH ₃ | CH ₃ | isomer I: m.p. 140-142°C |
| 2.002 | N | CH | OCH ₃ | OCH ₃ | CH ₃ | isomer II: m.p. 137-139°C |
| 2.003 | N | CH | OCH ₃ | OCHF ₂ | CH ₃ | |
| 2.004 | N | N | OCH ₃ | OCH ₃ | CH ₃ | |
| 2.005 | N | N | OCH ₃ | CH ₃ | CH ₃ | |
| 2.006 | N | N | OCH ₃ | N(CH ₃) ₂ | CH ₃ | |
| 2.007 | CH | N | OCH ₃ | OCH ₃ | CH ₃ | |
| 2.008 | CH | N | OCH ₃ | SCH ₃ | CH ₃ | |
| 2.009 | CH | N | OCH ₃ | CH ₃ | CH ₃ | |
| 2.010 | CH | N | OCH ₃ | CF ₃ | CH ₃ | |
| 2.011 | CH | N | OCH ₃ | Cl | CH ₃ | |
| 2.012 | N | N | OC ₂ H ₅ | NHCH ₃ | CH ₃ | |
| 2.013 | N | N | OC ₂ H ₅ | Δ | CH ₃ | |



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| Comp. No. | Y | Z | R ₃ | R ₄ | R | Phys. data |
|-----------|---|---|----------------|----------------|---|------------|
|-----------|---|---|----------------|----------------|---|------------|

**Table 3: Compounds of formula Ih**

(Ih)

| Comp. No. | X | R ₂ | R | A | Phys. data |
|-----------|---|----------------|---|---|------------|
|-----------|---|----------------|---|---|------------|

| | | | | | |
|-------|---|-----------------|-----------------|--|------------|
| 3.001 | S | CH ₃ | CH ₃ | | Example P9 |
|-------|---|-----------------|-----------------|--|------------|

| | | | | | |
|-------|---|-----------------|-----------------|--|-------------------------|
| 3.002 | O | CH ₃ | CH ₃ | | isomeric mixture: resin |
|-------|---|-----------------|-----------------|--|-------------------------|

| | | | | |
|-------|---|-----------------|-----------------|--------------------------------------|
| 3.003 | O | CH ₃ | CH ₃ | [Ala]-OC ₂ H ₅ |
|-------|---|-----------------|-----------------|--------------------------------------|

| | | | | |
|-------|---|-----------------|-----------------|--|
| 3.004 | O | CH ₃ | CH ₃ | [Val]-O-tert-C ₄ H ₉ |
|-------|---|-----------------|-----------------|--|

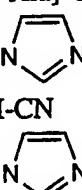
| | | | | |
|-------|---|-----------------|-----------------|------------------------|
| 3.005 | O | CH ₃ | CH ₃ | [Leu]-OCH ₃ |
|-------|---|-----------------|-----------------|------------------------|

| | | | | |
|-------|---|-----------------|-----------------|------------------------|
| 3.006 | O | CH ₃ | CH ₃ | [Phe]-OCH ₃ |
|-------|---|-----------------|-----------------|------------------------|

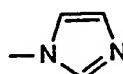
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| Comp. No. | X | R ₂ | R | A | Phys. data |
|-----------|---|-----------------|-----------------|---|---|
| 3.007 | O | CH ₃ | CH ₃ | [Me-Ala]-OCH ₃ | |
| 3.008 | O | CH ₃ | CH ₃ | [Ala]-OCH ₃ | mixture of 4 isomers: m.p. 114-118°C |
| 3.009 | O | CH ₃ | CH ₃ | [Ala]-O-tert-C ₄ H ₉ | |
| 3.010 | O | CH ₃ | CH ₃ | [Val]-OCH ₃ | |
| 3.011 | O | CH ₃ | CH ₃ | [Leu]-O-tert-C ₄ H ₉ | |
| 3.012 | O | CH ₃ | CH ₃ | [Me-Ala]-OH | |
| 3.013 | O | CH ₃ | CH ₃ | [Glu]-(OCH ₃) ₂ | |
| 3.014 | O | CH ₃ | CH ₃ | [Asp]-(OC ₂ H ₅) ₂ | |
| 3.015 | O | CH ₃ | CH ₃ | [Ala]-OH | |
| 3.016 | O | CH ₃ | CH ₃ | [Val]-OH | |
| 3.017 | O | CH ₃ | CH ₃ | [Leu]-OH | |
| 3.018 | O | CH ₃ | CH ₃ | [Ile]-OH | |
| 3.019 | O | CH ₃ | CH ₃ | | |
| 3.020 | O | CH ₃ | CH ₃ | | |
| 3.021 | O | CH ₃ | CH ₃ | [Glu]-(OCH ₂ CH=CH ₂) ₂ | |
| 3.022 | O | CH ₃ | CH ₃ | [Gly]-OH | |
| 3.023 | O | CH ₃ | CH ₃ | [Pro]-OH | |
| 3.024 | O | CH ₃ | CH ₃ | | |
| 3.025 | O | CH ₃ | CH ₃ | | |
| 3.026 | O | CH ₃ | CH ₃ | | |

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| Comp. No. | X | R ₂ | R | A | Phys. data |
|-----------|---|-----------------|---------------------------------|---|--|
| 3.027 | S | CH ₃ | CH ₃ | [Ala]-OCH ₃ | |
| 3.028 | S | CH ₃ | CH ₃ | [Val]-OCH ₃ | |
| 3.029 | S | CH ₃ | CH ₃ | [Me-Ala]-OCH ₃ | |
| 3.030 | S | CH ₃ | CH ₃ | [Leu]-OCH ₃ | oil (mixture of 4 isomers); ¹ H-NMR |
| 3.031 | S | CH ₃ | CH ₃ | [Ile]-OCH ₃ | |
| 3.032 | S | CH ₃ | CH ₂ CH ₃ | [Ala]-OCH ₃ | |
| 3.033 | S | CH ₃ | CH ₂ CH ₃ | [Me-Ala]-OCH ₃ | |
| 3.034 | S | CH ₃ | CH ₂ CH ₃ | [Leu]-OCH ₃ | |
| 3.035 | O | CH ₃ | CH ₂ CH ₃ | [Ala]-OCH ₃ | |
| 3.036 | O | CH ₃ | CH ₂ CH ₃ | [Val]-OCH ₃ | |
| 3.037 | O | CH ₃ | CH ₂ CH ₃ | [Me-Ala]-OCH ₃ | |
| 3.038 | O | CH ₃ | CH ₂ CH ₃ | [Leu]-OCH ₃ | |
| 3.039 | O | CH ₃ | CH ₂ CH ₃ | [Ile]-OCH ₃ | |
| 3.040 | O | CH ₃ | CH ₂ CH ₃ | [Ala]-OCH ₂ CH ₃ | |
| 3.041 | O | CH ₃ | CH ₂ CH ₃ | [Leu]-OCH ₂ CH ₃ | |
| 3.042 | O | CH ₃ | CH ₃ | [Ala][Ala]-OCH ₃ | |
| 3.043 | O | CH ₃ | CH ₃ | [Ala][Gly]-OCH ₃ | |
| 3.044 | O | CH ₃ | CH ₃ | [Leu][Gly]-OCH ₃ | |
| 3.045 | S | CH ₃ | H | [Ala]-OC ₂ H ₅ | oil (isomeric mixture) |
| 3.046 | S | CH ₃ | H | [Ala]-OCH ₃ | |
| 3.047 | S | CH ₃ | H | [Ala]-OH | |
| 3.048 | S | CH ₃ | H | [Val]-OH | |
| 3.049 | S | CH ₃ | H | [Leu]-OH | |
| 3.050 | S | CH ₃ | H | [Me-Ala]-OH | |
| 3.051 | S | CH ₃ | C ₂ H ₅ |  | isomer I: resin |
| 3.052 | S | CH ₃ | H | -NH-CN | m.p. 183-185°C |
| 3.053 | O | CH ₃ | C ₂ H ₅ |  | isomer I: ¹ H-NMR (300 MHz, CDCl ₃): 8.35 ppm (s, 1H), 7.62 ppm (d, 1H), |

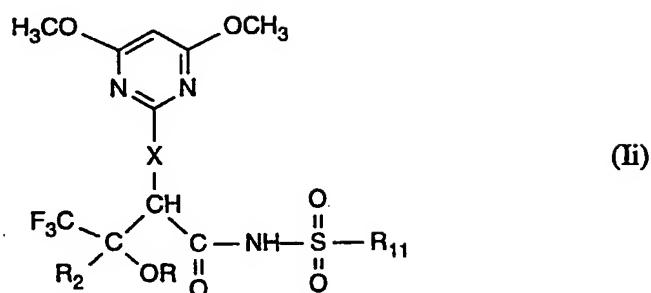
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| Comp. No. | X | R ₂ | R | A | Phys. data |
|-----------|---|-----------------|-------------------------------|---|---|
| 3.054 | O | CH ₃ | C ₂ H ₅ |  | 7.08 ppm (d, 1H), 5.85 ppm (s, 1H), 5.72 ppm (s, 1H), 3.62 ppm (s, 6H), 3.60 ppm (dxq, 2H), 1.78 ppm (s, 3H), 0.87 ppm (t, 3H). isomer II: ¹ H-NMR (300 MHz, CDCl ₃): 8.46 ppm (s, 1H), 7.68 ppm (d, 1H), 7.00 ppm (d, 1H), 5.70 ppm (s, 1H), 5.58 ppm (s, 1H), 3.77 ppm (s, 6H), 3.72 ppm (q, 2H), 1.70 ppm (s, 3H), 1.14 ppm (t, 3H). |
| 3.055 | O | CH ₃ | H | [Ala]-OCH ₃ | mixture of 4 isomers: oil |
| 3.056 | S | CH ₃ | H | NHOCH ₃ | isomer I: ¹ H-NMR (300 MHz, CDCl ₃): 9.43 ppm (broad signal, 1H), 6.23 ppm (broad signal, 1H), 5.72 ppm (s, 1H), 4.40 ppm (s, 1H), 3.95 ppm (s, 6H), 3.78 ppm (s, 3H), 1.55 ppm (s, 3H). |
| 3.057 | S | CH ₃ | H | NHOCH ₃ | isomer II: ¹ H-NMR (300 MHz, CDCl ₃): |

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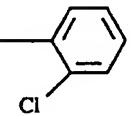
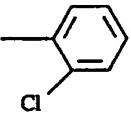
| Comp. No. | X | R ₂ | R | A | Phys. data |
|-----------|----|-----------------|---|-------------------------------------|--|
| 3.058 | S | CH ₃ | H | NHOH | 9.43 ppm (broad signal, 1H), 5.77 ppm (broad signal, 1H), 5.73 ppm (s, 1H), 4.65 ppm (s, 1H), 3.93 ppm (s, 6H), 3.78 ppm (s, 3H), 1.64 ppm (s, 3H). |
| 3.059 | O- | CH ₃ | H | NHOH | |
| 3.060 | S | CH ₃ | H | N(OCH ₃)CH ₃ | |
| 3.061 | O | CH ₃ | H | N(OCH ₃)CH ₃ | |

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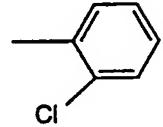
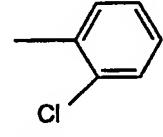
Table 4: Compounds of formula II

| Comp. No. | X | R ₂ | R | R ₁₁ | Phys. data |
|-----------|---|-----------------|-----------------|-------------------------------|---|
| 4.001 | O | CH ₃ | CH ₃ | CH ₃ | 1:1 isomeric mixture: ¹ H-NMR (300 MHz, CDCl ₃): 8.60 and 8.45 ppm (2 broad signals, NH), 5.80 and 5.78 ppm (2xs, 1H), 5.35 and 5.28 ppm (2xs, 1H), 3.92 ppm (s, 6H), 3.55 and 3.52 ppm (2xs, 3H), 3.28 and 3.24 ppm (2xs, 3H), 1.70 and 1.64 ppm (2xs, 3H). |
| 4.002 | S | CH ₃ | CH ₃ | CH ₃ | 1:2 isomeric mixture: ¹ H-NMR (300 MHz, CDCl ₃): 9.00 ppm (broad signal, 1H), 5.82 and 5.80 ppm (2xs, 1H), 4.92 and 4.70 ppm (2xs, 1H), 3.94 ppm (s, 6H), 3.55 and 3.51 ppm (2xs, 3H), 3.24 and 3.22 ppm (2xs, 3H), 1.72 and 1.68 ppm (2xs, 3H). |
| 4.003 | O | CH ₃ | CH ₃ | C ₂ H ₅ | |
| 4.004 | S | CH ₃ | CH ₃ | C ₂ H ₅ | |
| 4.005 | O | CH ₃ | CH ₃ | phenyl | |
| 4.006 | S | CH ₃ | CH ₃ | phenyl | |

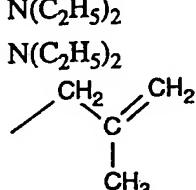
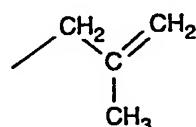
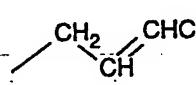
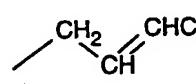
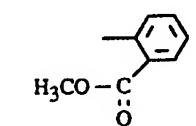
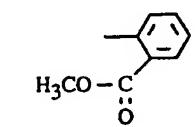
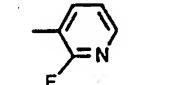
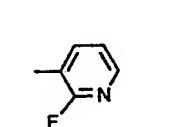
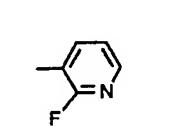
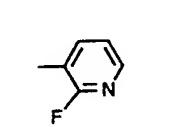
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| Comp. No. | X | R ₂ | R | R ₁₁ | Phys. data |
|-----------|---|-----------------|-----------------|---|--------------------------------------|
| 4.007 | O | CH ₃ | CH ₃ |  | |
| 4.008 | S | CH ₃ | CH ₃ |  | |
| 4.009 | O | CH ₃ | CH ₃ | CF ₃ | |
| 4.010 | S | CH ₃ | CH ₃ | CF ₃ | |
| 4.011 | O | CH ₃ | CH ₃ | N(CH ₃) ₂ | |
| 4.012 | S | CH ₃ | CH ₃ | N(CH ₃) ₂ | |
| 4.013 | O | CH ₃ | CH ₃ | N(C ₂ H ₅) ₂ | |
| 4.014 | S | CH ₃ | CH ₃ | N(C ₂ H ₅) ₂ | |
| 4.015 | O | CH ₃ | CH ₃ | cyclopropyl | |
| 4.016 | S | CH ₃ | CH ₃ | cyclopropyl | |
| 4.017 | O | CH ₃ | CH ₃ | cyclobutyl | |
| 4.018 | S | CH ₃ | CH ₃ | cyclobutyl | |
| 4.019 | O | CH ₃ | CH ₃ | 2-pyridyl | |
| 4.020 | S | CH ₃ | CH ₃ | 2-pyridyl | |
| 4.021 | O | CH ₃ | CH ₃ | NHCH ₂ CH ₃ | |
| 4.022 | S | CH ₃ | CH ₃ | NHCH ₂ CH ₃ | |
| 4.023 | O | CH ₃ | CH ₃ | NHCH ₂ CH ₂ CH ₃ | |
| 4.024 | S | CH ₃ | CH ₃ | NHCH ₂ CH ₂ CH ₃ | |
| 4.025 | O | CH ₃ | CH ₃ | NHCH ₂ C≡CH | |
| 4.026 | S | CH ₃ | CH ₃ | NHCH ₂ C≡CH | |
| 4.027 | O | CH ₃ | CH ₃ | N(OCH ₃)CH ₃ | |
| 4.028 | S | CH ₃ | CH ₃ | N(OCH ₃)CH ₃ | |
| 4.029 | O | CH ₃ | CH ₃ | 2-methyl-2-propenyl | 1:1 isomeric mixture: resin |
| 4.030 | S | CH ₃ | CH ₃ | 2-methyl-2-propenyl | 1:1 isomeric mixture; Example P12 |

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| Comp. No. | X | R ₂ | R | R ₁₁ | Phys. data |
|-----------|---|-----------------|-----------------|---|--|
| 4.031 | O | CH ₃ | CH ₃ | 3-chloro-2-propenyl | |
| 4.032 | S | CH ₃ | CH ₃ | 3-chloro-2-propenyl | |
| 4.033 | O | CH ₃ | CH ₃ | 2-chlorophenyl | |
| 4.034 | S | CH ₃ | CH ₃ | 2-chlorophenyl | |
| 4.035 | O | CH ₃ | CH ₃ | 2-methoxycarbonylphenyl | |
| 4.036 | S | CH ₃ | CH ₃ | 2-methoxycarbonylphenyl | |
| 4.037 | O | CH ₃ | H | CH ₃ | isomer II: m.p. 184-186°C; ¹ H-NMR (300 MHz, CDCl ₃): 10.8 ppm (broad signal, NH), 5.80 ppm (s, 1H), 5.26 ppm (s, 1H), 3.90 ppm (s, 6H), 3.23 ppm (s, 3H), 1.52 ppm (s, 3H). |
| 4.038 | S | CH ₃ | H | CH ₃ | m.p. 85°C (isomer I) |
| 4.039 | O | CH ₃ | H | C ₂ H ₅ | |
| 4.040 | S | CH ₃ | H | C ₂ H ₅ | |
| 4.041 | O | CH ₃ | H | phenyl | |
| 4.042 | S | CH ₃ | H | phenyl | |
| 4.043 | O | CH ₃ | H |  | |
| 4.044 | S | CH ₃ | H |  | |
| 4.045 | O | CH ₃ | H | CF ₃ | |
| 4.046 | S | CH ₃ | H | CF ₃ | |
| 4.047 | O | CH ₃ | H | N(CH ₃) ₂ | isomer II: m.p. 176-178°C |
| 4.048 | S | CH ₃ | H | N(CH ₃) ₂ | isomer I: resin |

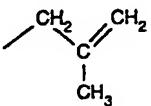
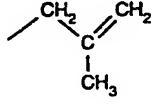
- 68 -

| Comp. No. | X | R ₂ | R | R ₁₁ | Phys. data |
|-----------|---|-----------------|-------------------------------|---|--|
| 4.049 | O | CH ₃ | H | N(C ₂ H ₅) ₂ | |
| 4.050 | S | CH ₃ | H | N(C ₂ H ₅) ₂ | |
| 4.051 | O | CH ₃ | H |  | |
| 4.052 | S | CH ₃ | H |  | |
| 4.053 | O | CH ₃ | H |  | |
| 4.054 | S | CH ₃ | H |  | |
| 4.055 | O | CH ₃ | H |  | |
| 4.056 | S | CH ₃ | H |  | |
| 4.057 | S | CH ₃ | C ₂ H ₅ |  | isomer I: m.p. 106-107°C |
| 4.058 | S | CH ₃ | C ₂ H ₅ |  | isomeric mixture 1:1 m.p. 103-106°C |
| 4.059 | S | CH ₃ | H |  | isomer I: m.p. 150-151°C |
| 4.060 | S | CH ₃ | H |  | isomeric mixture 2:3; |

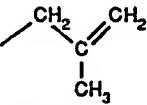
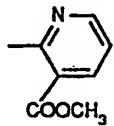
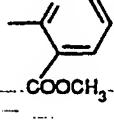
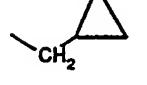
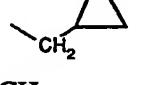
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| Comp. No. | X | R ₂ | R | R ₁₁ | Phys. data |
|-----------|---|-----------------|-------------------------------|---|--|
| 4.061 | S | CH ₃ | H |  | amorphous isomer I: m.p. 155°C |
| 4.062 | O | CH ₃ | H |  | isomer I: m.p. 80°C |
| 4.063 | S | CH ₃ | H |  | isomer I: m.p. 146-147°C |
| 4.064 | S | CH ₃ | C ₂ H ₅ | CH ₃ | 7:3 isomeric mixture: resin |
| 4.065 | O | CH ₃ | C ₂ H ₅ | CH ₃ | isomer I: ¹ H-NMR (300 MHz, CDCl ₃): 8.6 ppm (broad signal, NH), 5.80 ppm (s, 1H), 5.30 ppm (s, 1H), 3.92 ppm (s, 6H), 3.80 ppm (q, 2H), 3.28 ppm (s, 3H), 1.68 ppm (s, 3H), 1.30 ppm (t, 3H). |
| 4.066 | O | CH ₃ | C ₂ H ₅ | CH ₃ | 1:2 isomeric mixture: resin |
| 4.067 | O | CH ₃ | C ₂ H ₅ | N(CH ₃) ₂ | 3:2 isomeric mixture: resin |
| 4.068 | O | CH ₃ | H |  | isomer I: m.p. 179-180°C |
| 4.069 | O | CH ₃ | H |  | isomer I: m.p. 171-172°C |

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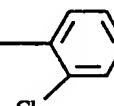
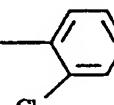
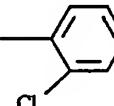
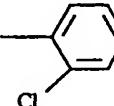
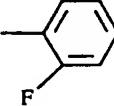
| Comp. No. | X | R ₂ | R | R ₁₁ | Phys. data |
|-----------|---|-----------------|-------------------------------|---|---|
| 4.070 | O | CH ₃ | C ₂ H ₅ |  | isomer II: ¹ H-NMR (300 MHz, CDCl ₃): 8.60 ppm (broad signal, NH), 5.80 ppm (s, 1H), 5.35 ppm (s, 1H), 5.08 and 5.00 ppm (2H), 4.08 ppm (m, 2H), 3.94 ppm (s, 6H), 3.75 ppm (q, 2H), 1.90 ppm (s, 3H), 1.62 ppm (s, 3H), 1.28 ppm (t, 3H). |
| 4.071 | O | CH ₃ | C ₂ H ₅ |  | isomer I: m.p. 123-124°C. |
| 4.072 | O | CH ₃ | H | N(CH ₃) ₂ | isomer I: m.p. 90-92°C |
| 4.073 | O | CH ₃ | H | CH ₃ | isomer I: ¹ H-NMR (300 MHz, CDCl ₃): 10.70 ppm (broad signal, NH), 5.75 ppm (s, 1H), 5.50 ppm (broad signal, OH), 5.32 ppm (s, 1H), 3.94 ppm (s, 6H), 3.26 ppm (s, 3H), 1.62 ppm (s, 3H). |
| 4.074 | S | CF ₃ | CH ₃ | CH ₃ | |

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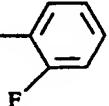
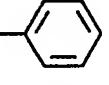
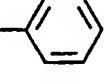
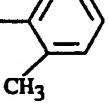
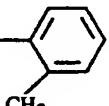
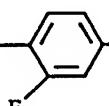
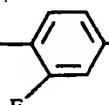
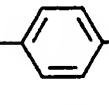
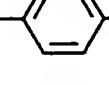
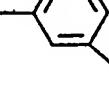
| Comp. No. | X | R ₂ | R | R ₁₁ | Phys. data |
|-----------|---|-----------------|-----------------|---|---|
| 4.075 | S | CF ₃ | CH ₃ |  | |
| 4.076 | S | CF ₃ | CH ₃ | N(CH ₃) ₂ | |
| 4.077 | S | CH ₃ | CH ₃ |  | |
| 4.078 | S | CF ₃ | CH ₃ |  | |
| 4.079 | S | CH ₃ | CH ₃ |  | |
| 4.080 | S | CF ₃ | CH ₃ |  | |
| 4.081 | S | CF ₃ | H | CH ₃ | m.p. 172-174°C |
| 4.082 | S | CF ₃ | H | N(CH ₃) ₂ | ¹ H-NMR (300 MHz, CDCl ₃): 9.82 ppm (broad signal, NH), 7.10 ppm (broad signal, OH), 5.88 ppm (s, 1H), 4.96 ppm (s, 1H), 3.95 ppm (s, 6H), 2.96 ppm (s, 6H). |

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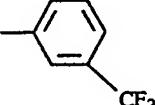
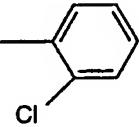
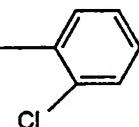
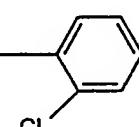
Table 5: Compounds of formula Ij

| Comp. No. | X | R ₂ | R ₁₂ | R ₁₃ | R | Phys. data | (Ij) | |
|-----------|---|-----------------|-----------------|---|-----------------|------------|-----------------|-----------------|
| | | | | | | | CH ₃ | CH ₃ |
| 5.001 | O | phenyl | H |  | CH ₃ | | | |
| 5.002 | O | phenyl | H |  | CH ₃ | | | |
| 5.003 | S | phenyl | H |  | CH ₃ | | | |
| 5.004 | O | CH ₃ | H |  | CH ₃ | | | |
| 5.005 | O | CH ₃ | H |  | CH ₃ | | | |
| 5.006 | S | CH ₃ | H |  | CH ₃ | | | |
| 5.007 | O | CH ₃ | H |  | CH ₃ | | | |

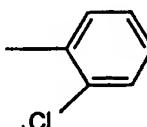
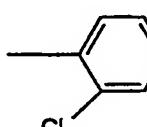
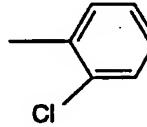
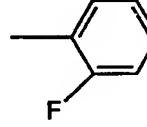
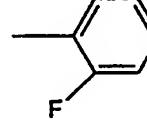
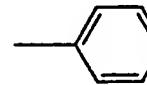
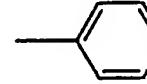
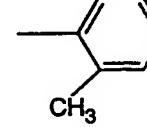
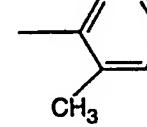
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| Comp. No. | X | R ₂ | R ₁₂ | R ₁₃ | R | Phys. data |
|-----------|---|-----------------|-----------------|---|-----------------|------------|
| 5.008 | S | CH ₃ | H |  | CH ₃ | |
| 5.009 | O | CH ₃ | H |  | CH ₃ | |
| 5.010 | S | CH ₃ | H |  | CH ₃ | |
| 5.011 | O | CH ₃ | H |  | CH ₃ | |
| 5.012 | S | CH ₃ | H |  | CH ₃ | |
| 5.013 | O | CH ₃ | H |  | CH ₃ | |
| 5.014 | S | CH ₃ | H |  | CH ₃ | |
| 5.015 | O | CH ₃ | H |  | CH ₃ | |
| 5.016 | S | CH ₃ | H |  | CH ₃ | |
| 5.017 | O | CH ₃ | H |  | CH ₃ | |

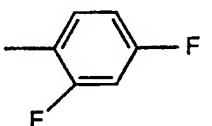
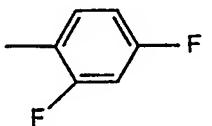
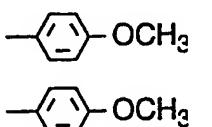
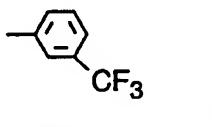
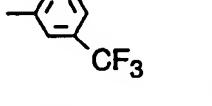
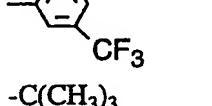
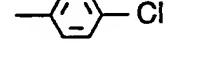
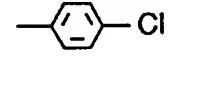
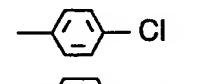
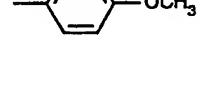
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| Comp. No. | X | R ₂ | R ₁₂ | R ₁₃ | R | Phys. data |
|-----------|---|-----------------|-----------------|---|-----------------|---|
| 5.018 | S | CH ₃ | H |  | CH ₃ | |
| 5.019 | O | CH ₃ | H | -C(CH ₃) ₃ | CH ₃ | |
| 5.020 | S | CH ₃ | H | -C(CH ₃) ₃ | CH ₃ | 1:1 isomeric mixture: H ¹ -NMR (CDCl ₃ , 300 MHz): 7.80 and 7.72 ppm (2xbroad signal, 1H), 5.78 and 5.76 ppm (2xs, 1H), 4.96 and 4.77 ppm (2xs, 1H), 4.60 ppm (broad signal, 1H), 3.92 ppm (s, 6H), 3.49 and 3.45 ppm (s, 3H), 1.73 and 1.68 ppm (2xs, 3H), 1.08 and 1.02 ppm (2xs, 9H). |
| 5.021 | O | CH ₃ | CH ₃ | CH ₃ | CH ₃ | |
| 5.022 | S | CH ₃ | CH ₃ | CH ₃ | CH ₃ | |
| 5.023 | O | phenyl | H |  | H | isomer I: Example P11 m.p. 193-194°C |
| 5.024 | O | phenyl | H |  | H | isomer II: Example P11 crystalline, amorphous |
| 5.025 | S | phenyl | H |  | H | |

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| Comp. No. | X | R ₂ | R ₁₂ | R ₁₃ | R | Phys. data |
|-----------|---|-----------------|-----------------|---|---|---|
| 5.026 | O | CH ₃ | H |  | H | isomer I: m.p. 195-197°C |
| 5.027 | O | CH ₃ | H |  | H | isomer II: m.p. 194-195°C |
| 5.028 | S | CH ₃ | H |  | H | |
| 5.029 | O | CH ₃ | H |  | H | |
| 5.030 | S | CH ₃ | H |  | H | 3:2 isomeric mixture: m.p. 151-155°C |
| 5.031 | O | CH ₃ | H |  | H | |
| 5.032 | S | CH ₃ | H |  | H | |
| 5.033 | O | CH ₃ | H |  | H | |
| 5.034 | S | CH ₃ | H |  | H | |

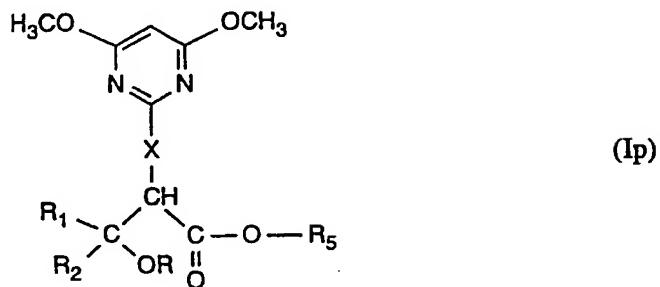
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| Comp. No. | X | R ₂ | R ₁₂ | R ₁₃ | R | Phys. data |
|-----------|---|-----------------|-----------------|---|-----------------|---|
| 5.035 | O | CH ₃ | H |  | H | |
| 5.036 | S | CH ₃ | H |  | H | |
| 5.037 | O | CH ₃ | H |  | H | |
| 5.038 | S | CH ₃ | H |  | H | |
| 5.039 | O | CH ₃ | H |  | | |
| 5.040 | S | CH ₃ | H |  | H | |
| 5.041 | O | CH ₃ | H | -C(CH ₃) ₃ | H | |
| 5.042 | S | CF ₃ | H | -C(CH ₃) ₃ | H | |
| 5.043 | S | CH ₃ | H | -C(CH ₃) ₃ | H | isomer I: m.p. 121-122°C |
| 5.044 | S | CH ₃ | H | -C(CH ₃) ₃ | H | isomer II: m.p. 145-147°C |
| 5.045 | O | CH ₃ | CH ₃ | CH ₃ | H | |
| 5.046 | S | CH ₃ | CH ₃ | CH ₃ | H | |
| 5.047 | S | CH ₃ | H |  | H | isomer I: m.p. 134-136°C |
| 5.048 | S | CH ₃ | H |  | H | isomer II: m.p. 136-139°C |
| 5.049 | S | CF ₃ | H |  | CH ₃ | |
| 5.050 | S | CF ₃ | H |  | CH ₃ | ¹ H-NMR (300 MHz, CDCl ₃): 8.40 ppm |

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| Comp. No. | X | R ₂ | R ₁₂ | R ₁₃ | R | Phys. data |
|-----------|---|-----------------|-----------------|----------------------------------|-----------------|---|
| 5.051 | S | CF ₃ | H | C(CH ₃) ₃ | CH ₃ | <p>(d, NH), 6.68 ppm (d, 2H), 6.61 ppm (d, 2H), 5.92 ppm (d, NH), 5.84 ppm (s, 1H), 5.39 ppm (s, 1H), 3.87 ppm (s, 6H), 3.78 ppm (s, 3H), 3.72 ppm (s, 3H); m.p. 157-158.5°C</p> <p>¹H-NMR (300 MHz, CDCl₃): 7.88 ppm (broad signal, NH), 5.80 ppm (s, 1H), 5.44 ppm (s, 1H), 4.62 ppm (broad signal, NH), 3.94 ppm (s, 6H), 3.78 ppm (s, 3H), 1.00 ppm (s, 9H).</p> |
| 5.052 | S | CF ₃ | H | | H | <p>¹H-NMR (300 MHz, CDCl₃): 8.98 ppm (d, NH), 7.70 ppm (s, OH), 6.76 ppm (d, 2H), 6.66 ppm (d, 2H), 5.98 ppm (d, NH), 5.88 ppm (s, 1H), 5.25 ppm (s, 1H), 3.89 ppm (s, 6H), 3.75 ppm (s, 6H).</p> |

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Table 6: Compounds of formula I_p:

| Comp. No. | X | R ₁ | R ₂ | R | R ₅ | Phys. data |
|--------------|---|-----------------|-----------------|---------------------------------|----------------------------------|--|
| 6.001 | S | CF ₃ | CH ₃ | CH ₃ | C(CH ₃) ₃ | isomer I: ¹ H-NMR (300 MHz, CDCl ₃): Example P5; 5.78 ppm (s, 1H), 5.24 ppm (s, 1H), 3.94 ppm (s, 6H), 3.50 ppm (s, 3H), 1.71 ppm (s, 3H), 1.45 ppm (s, 9H). |
| 6.002 | S | CF ₃ | CH ₃ | CH ₃ | C(CH ₃) ₃ | isomer II: ¹ H-NMR (300 MHz, CDCl ₃): Example P5; 5.76 ppm (s, 1H), 5.16 ppm (s, 1H), 3.94 ppm (s, 6H), 3.45 ppm (s, 3H), 1.62 ppm (s, 3H), 1.43 ppm (s, 9H). |
| 6.003 | S | CF ₃ | CH ₃ | CH ₂ CH ₃ | C(CH ₃) ₃ | isomer I: ¹ H-NMR (300 MHz, CDCl ₃): 5.78 ppm (s, 1H), 5.25 ppm (s, 1H), 3.97 ppm (s, 6H), 3.72 ppm (q, 2H), 1.72 ppm (s, 3H), 1.49 ppm (s, 9H). |
| 6.004 | S | CF ₃ | CH ₃ | CH ₂ CH ₃ | C(CH ₃) ₃ | isomer II: ¹ H-NMR (300 MHz, CDCl ₃): 5.76 ppm (s, 1H), 5.17 ppm (s, 1H), 3.94 ppm (s, 6H), 3.70 ppm (q, 2H), |

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| Comp. No. | X | R ₁ | R ₂ | R | R ₅ | Phys. data |
|--------------|---|-----------------|-----------------|---------------------------------|----------------------------------|---|
| 6.005 | O | CF ₃ | CH ₃ | CH ₃ | C(CH ₃) ₃ | 1.62 ppm (s, 3H), 1.45 ppm (s, 9H). isomer I: oil; ¹ H-NMR (300 MHz, CDCl ₃): 5.74 ppm (s, 1H), 5.30 ppm (s, 1H), 3.93 ppm (s, 6H), 3.52 ppm (s, 3H), 1.67 ppm (s, 3H), 1.46 ppm (s, 9H). |
| 6.006 | O | CF ₃ | CH ₃ | CH ₃ | C(CH ₃) ₃ | isomer II: oil; ¹ H-NMR (300 MHz, CDCl ₃): 5.72 ppm (s, 1H), 5.25 ppm (s, 1H), 3.92 ppm (s, 6H), 3.52 ppm (s, 3H), 1.65 ppm (s, 3H), 1.42 ppm (s, 9H). |
| 6.007 | O | CF ₃ | CH ₃ | CH ₂ CH ₃ | C(CH ₃) ₃ | isomer I: m.p. 84-86°C |
| 6.008 | O | CF ₃ | CH ₃ | CH ₂ CH ₃ | C(CH ₃) ₃ | isomer II: oil; ¹ H-NMR (300 MHz, CDCl ₃): 5.75 ppm (s, 1H), 5.26 ppm (s, 1H), 3.93 ppm (s, 6H), 3.76 ppm (m, 2H), 1.67 ppm (s, 3H), 1.42 ppm (s, 9H), 1.20 ppm (t, 3H). |
| 6.009 | O | CF ₃ | CH ₃ | SO ₂ CH ₃ | C(CH ₃) ₃ | isomer I: ¹ H-NMR (300 MHz, CDCl ₃): 5.78 ppm (s, 1H), 5.62 ppm (s, 1H), 3.91 ppm (s, 6H), 3.20 ppm (s, 3H), 2.13 ppm (s, 3H), 1.43 ppm (s, 9H). |
| 6.010 | S | CF ₃ | CH ₃ | SO ₂ CH ₃ | C(CH ₃) ₃ | isomeric mixture: ¹ H-NMR (300 MHz, CDCl ₃): 5.80 ppm (s, 1H), 5.52 and 5.42 ppm (2xs, 1H), 3.96 and 3.94 ppm (2xs, 6H), 3.18 and 3.04 ppm |

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| Comp. No. | X | R ₁ | R ₂ | R | R ₅ | Phys. data |
|--------------|---|-----------------|---|---------------------------------|---|--|
| 6.011 | O | CF ₃ |  | SO ₂ CH ₃ | C(CH ₃) ₃ | (2xs, 3H), 2.17 and 2.14 ppm (2xs, 3H), 1.46 ppm (s, 9H). isomer I: Example P3 |
| 6.012 | O | CF ₃ |  | SO ₂ CH ₃ | C(CH ₃) ₃ | isomer II: Example P3 |
| 6.013 | S | CF ₃ | CH ₃ | CH ₃ | CH ₃ | isomeric mixture: H ¹ -NMR (300 MHz, CDCl ₃): 5.75 and 5.73 ppm (2xs, 1H), 5.28 and 5.18 ppm (2xs, 1H), 3.94 ppm (s, 6H), 3.65 and 3.63 ppm (2xs, 3H), 3.49 and 3.46 ppm (2xs, 3H), 1.72 and 1.62 ppm (2xs, 3H). |
| 6.014 | S | CF ₃ | CH ₃ | CH ₃ | CH ₂ CH ₃ | |
| 6.015 | S | CF ₃ | CH ₃ | CH ₃ | CH ₂ CH=CH ₂ | |
| 6.016 | S | CF ₃ | CH ₃ | CH ₃ | CH ₂ CH≡CH | |
| 6.017 | S | CF ₃ | CH ₃ | CH ₃ | CH ₂ OCOC(CH ₃) ₃ | |
| 6.018 | S | CF ₃ | CH ₃ | CH ₃ | CH(CH ₃)OCOEt | |
| 6.019 | S | CF ₃ | CH ₃ | CH ₃ | CH(CH ₃)OCOOEt | |
| 6.020 | S | CF ₃ | CH ₃ | CH ₃ | benzyl | |
| 6.021 | O | CF ₃ | CH ₃ | CH ₃ | CH ₃ | |
| 6.022 | O | CF ₃ | CH ₃ | CH ₃ | CH ₂ CH ₃ | |
| 6.023 | O | CF ₃ | CH ₃ | CH ₃ | CH ₂ CH=CH ₂ | 1:3 isomeric mixture; m.p. 86-91°C |
| 6.024 | O | CF ₃ | CH ₃ | CH ₃ | CH ₂ CH≡CH | |
| 6.025 | O | CF ₃ | CH ₃ | CH ₃ | CH ₂ OCOC(CH ₃) ₃ | |
| 6.026 | O | CF ₃ | CH ₃ | CH ₃ | CH(CH ₃)OCOEt | |
| 6.027 | O | CF ₃ | CH ₃ | CH ₃ | CH(CH ₃)COOEt | |
| 6.028 | O | CF ₃ | CH ₃ | CH ₃ | benzyl | |
| 6.029 | S | CF ₃ | CH ₃ | H | -C ₂ H ₅ | oil; MS: M ⁺ 370 (8), 325 (4), 301 (12), 258 (34), 212 (31), |

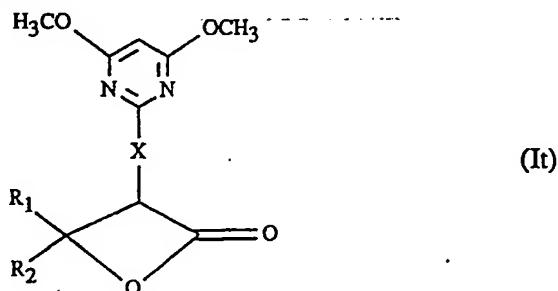
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| Comp. No. | X | R ₁ | R ₂ | R | R ₅ | Phys. data |
|--------------|---|-----------------|-----------------|------------------------------------|--|---|
| 6.030 | S | CF ₃ | CH ₃ | H | -CH ₃ | 185 (100). 1:1 isomeric mixture; oil; MS: M ⁺ 356 (58), 325 (8), 287 (34), 244 (48), 212 (27), 185 (100). |
| 6.031 | S | CF ₃ | CH ₃ | H | CH ₂ CH ₂ O-N=C(CH ₃) ₂ | oil; ¹ H-NMR (300 MHz, CDCl ₃): 5.82 and 5.79 ppm (2s, 1H), 5.52 and 5.27 ppm (2s, 1H), 4.96 ppm (broad signal, 1H), 4.5-4.3 ppm (4H), 3.95 ppm (s, 6H), 1.9-1.8 ppm (4s, 6H), 1.62 and 1.56 ppm (2s, 3H). |
| 6.032 | O | CF ₃ | CH ₃ | H | N(CH ₃) ₂ | isomer I: m.p. 153-154°C |
| 6.033 | O | CF ₃ | CH ₃ | H | N(CH ₃) ₂ | isomer II: m.p. 117-119°C |
| 6.034 | O | CF ₃ | CH ₃ | H | CH ₂ CH=CH ₂ | 1:3 isomeric mixture: ¹ H-NMR (300 MHz, CDCl ₃): 5.85 ppm (m, 1H), 5.78 ppm (s, 1H), 5.33 ppm (s, 1H), 5.40-5.30 ppm (m, 2H), 4.66 ppm (m, 2H), 3.92 ppm (s, 6H), 1.65 and 1.53 ppm (2xs, 3H). |
| 6.035 | O | CF ₃ | CH ₃ | CH ₂ CH=CH ₂ | C(CH ₃) ₃ | isomer I: m.p. 72-74°C |
| 6.036 | O | CF ₃ | CH ₃ | benzyl | C(CH ₃) ₃ | 2:1 isomeric mixture: ¹ H-NMR (300 MHz, CDCl ₃): 7.40-7.20 ppm (5H), 5.72 ppm (s, 1H), 5.42 and 5.33 ppm (2xs, 1H), 4.30 ppm (m, 2H), 3.94 ppm (s, 6H), 1.78 and 1.74 ppm (2xs, 3H), 1.42 and 1.33 ppm (2xs, 9H). |
| 6.037 | O | CF ₃ | CF ₃ | CH ₃ | C(CH ₃) ₃ | |

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| Comp. No. | X | R ₁ | R ₂ | R | R ₅ | Phys. data |
|-----------|---|-----------------|-----------------|-----------------|---|--|
| 6.038 | S | CF ₃ | CF ₃ | CH ₃ | C(CH ₃) ₃ | m.p. 84-85°C |
| 6.039 | S | CF ₃ | CF ₃ | CH ₃ | CH ₂ OCOC(CH ₃) ₃ | ¹ H-NMR (300 MHz, CDCl ₃): 5.81 ppm (dxd, 2H), 5.79 ppm (s, 1H), 5.70 ppm (s, 1H), 3.92 ppm (s, 6H), 3.72 ppm (s, 3H), 1.16 ppm (s, 9H). |

Table 7: Compounds of formula I

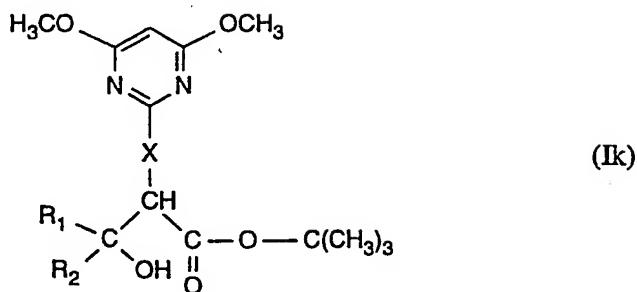


| Comp. No. | X | R ₁ | R ₂ | Phys. data |
|-----------|---|-------------------------------|-----------------|--|
| 7.001 | O | CF ₃ | CH ₃ | isomer I: m.p. 69-70°C |
| 7.002 | S | CF ₃ | CH ₃ | isomer I: m.p. 73-74°C |
| 7.003 | S | CF ₃ | CH ₃ | isomer II: ¹ H-NMR (300 MHz, CDCl ₃): 6.05 ppm (s, 1H), 5.97 ppm (s, 1H), 3.92 ppm (s, 6H), 1.95 ppm (s, 3H). |
| 7.004 | O | CF ₃ | | 1:1 isomeric mixture; m.p. 100-106°C (Example P10) |
| 7.005 | S | CF ₃ | | |
| 7.006 | O | C ₂ F ₅ | CH ₃ | |
| 7.007 | S | C ₂ F ₅ | CH ₃ | |
| 7.008 | O | C ₃ F ₇ | CH ₃ | |
| 7.009 | S | C ₃ F ₇ | CH ₃ | |

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| Comp.No. | X | R ₁ | R ₂ | Phys. data |
|----------|---|-----------------|-------------------------------|--|
| 7.010 | O | CF ₃ | C ₂ H ₅ | |
| 7.011 | S | CF ₃ | C ₂ H ₅ | |
| 7.012 | S | CH ₃ | C ₂ H ₅ | 1:1 isomeric mixture; IR (KBr) 1823 cm ⁻¹ ; ¹ H-NMR (300 MHz, CDCl ₃): 5.79 ppm (s, 1H), 5.52 ppm (s, 1H), 3.94 ppm (s, 6H), 2.1-1.8 ppm (m, 2H), 1.75 and 1.58 ppm (2xs, 3H), 1.09 and 1.02 ppm (2xt, 3H). |
| 7.013 | O | CF ₃ | CH ₃ | isomer II: ¹ H-NMR (300 MHz, CDCl ₃): 6.20 ppm (s, 1H), 5.85 ppm (s, 1H), 3.96 ppm (s, 6H), 1.95 ppm (s, 3H). m.p. 108-110°C |
| 7.014 | S | CF ₃ | CF ₃ | ¹ H-NMR (300 MHz, CDCl ₃): 7.10 ppm (s, 1H), 5.88 ppm (s, 1H), 3.92 ppm (s, 6H); Example P13. |
| 7.015 | O | CH ₃ | CH ₃ | ¹ H-NMR (300 MHz, CDCl ₃): 5.81 ppm (s, 1H), 5.78 ppm (s, 1H), 3.95 ppm (s, 6H), 1.68 ppm (s, 3H), 1.57 ppm (s, 3H). |
| 7.016 | S | CH ₃ | CH ₃ | ¹ H-NMR (300 MHz, CDCl ₃): 5.81 ppm (s, 1H), 5.42 ppm (s, 1H), 3.93 ppm (s, 6H), 1.80 ppm (s, 3H), 1.62 ppm (s, 6H). |

Table 8: Compounds of formula IIk

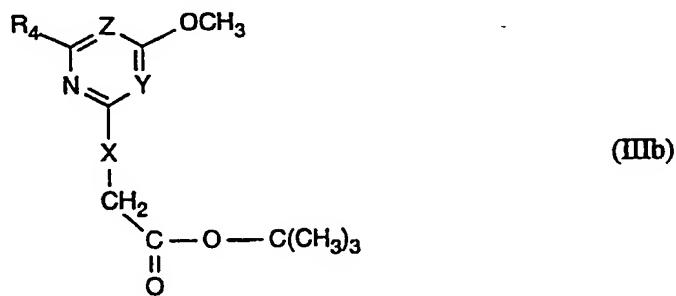


| Comp. No. | X | R ₁ | R ₂ | Phys. data |
|-----------|---|-------------------------------|-------------------------------|--|
| 8.001 | S | CF ₃ | CH ₃ | isomer I: ¹ H-NMR (300 MHz, CDCl ₃): 5.80 ppm (s, 1H), 5.23 ppm (broad signal, 1H), 5.04 ppm (s, 1H). |
| 8.002 | S | CF ₃ | CH ₃ | isomer II: m.p. 95-97°C |
| 8.003 | S | CF ₃ | phenyl | isomer I: m.p. 110-111°C |
| 8.004 | S | CF ₃ | phenyl | isomer II: m.p. 85-86°C |
| 8.005 | O | CF ₃ | CH ₃ | Example P2; isomer I: m.p. 135-137°C |
| 8.006 | O | CF ₃ | phenyl | 2:1 isomeric mixture ¹ H-NMR (300 MHz, CDCl ₃): 5.78 and 6.00 ppm (2xs, 1H), 5.72 and 5.75 ppm (2xs, 1H), 4.30 and 4.52 ppm (2xs, 1H), 1.07 and 1.22 ppm (2xs, 9H). |
| 8.007 | O | CH ₃ | CH ₃ | m.p. 87-89°C |
| 8.009 | O | CH ₃ | C ₂ H ₅ | m.p. 82-84°C |
| 8.010 | O | C ₂ H ₅ | CH ₃ | m.p. 86-87°C |
| 8.011 | O | CF ₃ | CH ₃ | Example P2; isomer II: m.p. 69-70°C |
| 8.012 | S | CH ₃ | phenyl | isomer I: m.p. 66-67°C |
| 8.013 | S | CH ₃ | phenyl | isomer II: oil; ¹ H-NMR (300 MHz, CDCl ₃): 7.55 ppm (d, 2H), 7.32 ppm (t, 2H), 7.24 ppm (t, 1H), 5.72 ppm (s, 1H), 4.96 ppm (s, 1H), 4.38 ppm (broad signal, 1H), 3.94 ppm (s, 6H), 1.80 ppm (s, 3H), 0.90 ppm (s, 9H). |

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| Comp. No. | X | R ₁ | R ₂ | Phys. data |
|-----------|---|-----------------|---|---|
| 8.014 | S | CH ₃ |  | isomeric mixture: ¹ H-NMR (300 MHz, CDCl ₃): 5.75 ppm (s, 1H), 4.72 and 4.68 ppm (2xs, 1H), 3.95 ppm (s, 6H), 3.52 and 3.30 ppm (2xs, 1H), 1.48 ppm (s, 9H), 1.35 ppm (s, 3H), 1.10 ppm (broad signal, 1H), 0.43 ppm (broad signal, 4H). |
| 8.015 | S | | -(CH ₂) ₄ - | m.p. 60.0-60.5°C |
| 8.016 | S | CF ₃ | CF ₃ | ¹ H-NMR (300 MHz, CDCl ₃): 5.86 ppm (s, 1H), 5.06 ppm (s, 1H), 3.94 ppm (s, 6H), 1.51 ppm (s, 9H). |

Table 9: Compounds of formula IIIb



| Comp. No. | X | Y | Z | R ₄ | Phys. data |
|-----------|---|----|----|-------------------------------------|--|
| 9.001 | S | N | CH | OCH ₃ | b.p. 130°C/1x10 ⁻³ torr (Example P7) |
| 9.002 | O | N | CH | OCH ₃ | m.p. 63-64.5°C (Example P1) |
| 9.003 | S | N | N | OCH ₃ | |
| 9.004 | O | N | N | OCH ₃ | |
| 9.005 | S | CH | N | OCH ₃ | |
| 9.006 | O | CH | N | OCH ₃ | |
| 9.007 | S | N | | -CH ₂ CH ₂ O- | |
| 9.008 | O | N | | -CH ₂ CH ₂ O- | |

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Formulation examples for compounds of formula I (throughout, percentages are by weight)

F1. Emulsifiable concentrates

| | a) | b) | c) | d) |
|--|------|------|------|------|
| a compound of Tables 1-8 | 5 % | 10 % | 25 % | 50 % |
| calcium dodecylbenzene-sulfonate | 6 % | 8 % | 6 % | 8 % |
| castor oil polyglycol ether (36 mol of ethylene oxide) | 4 % | - | 4 % | 4 % |
| octylphenol polyglycol ether (7-8 mol of ethylene oxide) | - | 4 % | - | 2 % |
| cyclohexanone | - | - | 10 % | 20 % |
| aromatic hydrocarbon mixture C ₉ -C ₁₂ | 85 % | 78 % | 55 % | 16 % |

Emulsions of any desired concentration can be produced from such concentrates by dilution with water.

F2. Solutions

| | a) | b) | c) | d) |
|--|------|------|------|------|
| a compound of Tables 1-8 | 5 % | 10 % | 50 % | 90 % |
| dipropylene glycol methyl ether | - | 20 % | 20 % | - |
| polyethylene glycol mol. wt. 400 | 20 % | 10 % | - | - |
| N-methyl-2-pyrrolidone | - | - | 30 % | 10 % |
| aromatic hydrocarbon mixture C ₉ -C ₁₂ | 75 % | 60 % | - | - |

These solutions are suitable for application in the form of micro-drops.

F3. Wettable powders

| | a) | b) | c) | d) |
|--|-----|------|------|------|
| a compound of Tables 1-8 | 5 % | 25 % | 50 % | 80 % |
| sodium lignosulfonate | 4 % | - | 3 % | - |
| sodium lauryl sulfate | 2 % | 3 % | - | 4 % |
| sodium diisobutylnaphthalene sulfonate | - | 6 % | 5 % | 6 % |
| octylphenol polyglycol ether (7-8 mol of ethylene oxide) | - | 1 % | 2 % | - |

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| | | | | |
|-------------------------------|------|------|------|------|
| highly dispersed silicic acid | 1 % | 3 % | 5 % | 10 % |
| kaolin | 88 % | 62 % | 35 % | - |

The active ingredient is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders which can be diluted with water to give suspensions of the desired concentration.

F4. Coated granules

| | | | |
|---|--------|------|------|
| a compound of Tables 1-8 | a) | b) | c) |
| highly dispersed silicic acid | 0.1 % | 5 % | 15 % |
| inorganic carrier | 0.9 % | 2 % | 2 % |
| (diameter 0.1 - 1 mm) | 99.0 % | 93 % | 83 % |
| such as CaCO_3 or SiO_2 | | | |

The active ingredient is dissolved in methylene chloride, the solution is sprayed onto the carrier, and the solvent is subsequently evaporated off *in vacuo*.

F5. Coated granules

| | | | |
|---|--------|------|------|
| a compound of Tables 1-8 | a) | b) | c) |
| polyethylene glycol mol. wt. 200 | 0.1 % | 5 % | 15 % |
| highly dispersed silicic acid | 1.0 % | 2 % | 3 % |
| inorganic carrier | 0.9 % | 1 % | 2 % |
| (diameter 0.1 - 1 mm) | 98.0 % | 92 % | 80 % |
| such as CaCO_3 or SiO_2 | | | |

The finely ground active ingredient is uniformly applied, in a mixer, to the carrier moistened with polyethylene glycol. Non-dusty coated granules are obtained in this manner.

F6. Extruder granules

| | | | | |
|--------------------------|--------|------|------|------|
| a compound of Tables 1-8 | a) | b) | c) | d) |
| sodium lignosulfonate | 0.1 % | 3 % | 5 % | 15 % |
| carboxymethylcellulose | 1.5 % | 2 % | 3 % | 4 % |
| kaolin | 1.4 % | 2 % | 2 % | 2 % |
| | 97.0 % | 93 % | 90 % | 79 % |

The active ingredient is mixed and ground with the adjuvants, and the mixture is

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moistened with water. The mixture is extruded and then dried in a stream of air.

F7. Dusts

| | a) | b) | c) |
|--------------------------|--------|------|------|
| a compound of Tables 1-8 | 0.1 % | 1 % | 5 % |
| talcum | 39.9 % | 49 % | 35 % |
| kaolin | 60.0 % | 50 % | 60 % |

Ready-for-use dusts are obtained by mixing the active ingredient with the carriers and grinding the mixture in a suitable mill.

F8. Suspension concentrates

| | a) | b) | c) | d) |
|--|-------|-------|-------|-------|
| a compound of Tables 1-8 | 3 % | 10 % | 25 % | 50 % |
| ethylene glycol | 5 % | 5 % | 5 % | 5 % |
| nonylphenol polyglycol ether (15 mol of ethylene oxide) | - | 1 % | 2 % | - |
| sodium lignosulfonate | 3 % | 3 % | 4 % | 5 % |
| carboxymethylcellulose | 1 % | 1 % | 1 % | 1 % |
| 37% aqueous formaldehyde solution | 0.2 % | 0.2 % | 0.2 % | 0.2 % |
| silicone oil emulsion | 0.8 % | 0.8 % | 0.8 % | 0.8 % |
| water | 87 % | 79 % | 62 % | 38 % |

The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired concentration can be obtained by dilution with water.

Biological Examples:

Example B1: Preemergence herbicidal action

Monocotyledonous and dicotyledonous test plants are sown in plastic pots containing standard soil and, immediately after sowing, are sprayed with an aqueous suspension of the test compounds, prepared from a 25 % wettable powder formulation (Formulation example F3 b)), corresponding to a rate of application of 2 kg of active ingredient/hectare (500 l of water/ha). The test plants are then cultivated in a greenhouse under optimum conditions. After 3 weeks, the test is evaluated in accordance with a scale of nine ratings (1 = total damage, 9 = no action). Ratings of 1 to 4 (especially 1 to 3) indicate good to

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very good herbicidal action.

Test plants: Setaria, Cyperus, Sinapis, Stellaria, Solanum, Ipomoea.

The compounds of Tables 1 to 8 exhibit pronounced herbicidal action in this test.

Examples of the good herbicidal action are listed in Table B1.

Table B1: Preemergence action

| Test plants: Compound No. | Seta- ria | Cy- perus | Sina- pis | Stel- laria | Sola- num | Ipo- moea |
|----------------------------------|--------------|--------------|--------------|----------------|--------------|--------------|
| 1.001 (isomer I) | 1 | 2 | 2 | 2 | 2 | 2 |
| 1.002 (isomer II) | 1 | 1 | 2 | 1 | 2 | 2 |
| 1.065 (isomer I) | 2 | 1 | 2 | 2 | 2 | 3 |
| 1.065 (isomer II) | 1 | 2 | 2 | 2 | 2 | 2 |
| 1.066 (isomer I) | 1 | 1 | 2 | 2 | 2 | 2 |
| 1.088 + 1.089 (isomer I + II) | 3 | 2 | 5 | 2 | 2 | 3 |
| 1.088 (isomer I) | 4 | 1 | 2 | 2 | 2 | 2 |
| 1.089 (isomer II) | 1 | 1 | 3 | 2 | 2 | 2 |
| 2.001 (isomer I) | 1 | 2 | 2 | 2 | 2 | 3 |
| 2.002 (isomer II) | 2 | 2 | 2 | 2 | 2 | 3 |
| 3.051 (isomer I) | 2 | 1 | 2 | 2 | 2 | 2 |

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| Test plants: Compound No. | Seta- ria | Cy- perus | Sina- pis | Stel- laria | Sola- num | Ipo- moea |
|------------------------------|--------------|--------------|--------------|----------------|--------------|--------------|
| 4.002 (isomeric mixture) | 2 | 2 | 2 | 2 | 2 | 2 |
| 4.064 (isomeric mixture) | 2 | 2 | 2 | 3 | 2 | 3 |
| 4.065 (isomer I) | 2 | 2 | 2 | 2 | 2 | 3 |
| 4.066 (isomeric mixture) | 2 | 2 | 2 | 3 | 2 | 2 |
| 4.067 (isomeric mixture) | 2 | 2 | 2 | 2 | 3 | 3 |
| 5.020 (isomeric mixture) | 2 | 1 | 2 | 1 | 1 | 2 |
| 5.043 (isomer I) | 1 | 1 | 3 | 2 | 2 | 3 |
| 5.044 (isomer II) | 1 | 1 | 3 | 2 | 2 | 2 |
| 5.047 (isomer I) | 2 | 1 | 2 | 2 | 2 | 2 |
| 5.048 (isomer II) | 2 | 1 | 3 | 2 | 2 | 2 |
| 7.002 (isomer I) | 1 | 1 | 2 | 2 | 2 | 2 |

The same results are obtained when the compounds of formula I are formulated in accordance with Examples F1, F2 and F4 to F8.

Example B2: Post-emergence herbicidal action (contact herbicide)

Monocotyledonous and dicotyledonous test plants are raised in a greenhouse in plastic pots containing standard soil and in the 4- to 6-leaf stage are sprayed with an aqueous suspension of the test compounds of formula I, prepared from a 25 % wettable powder formulation (Formulation example F3 b)), corresponding to a rate of application of 2 kg of active ingredient/hectare (500 l of water/ha). The test plants are then grown on in the greenhouse under optimum conditions. After about 18 days the test is evaluated in accordance with a scale of nine ratings (1 = total damage, 9 = no action). Ratings of 1 to 4 (especially 1 to 3) indicate good to very good herbicidal action.

Test plants: Setaria, Sinapis, Stellaria, Solanum, Ipomoea.

The compounds of Tables 1 to 8 exhibit pronounced herbicidal action in this test.

Examples of the good herbicidal activity are shown in Table B2.

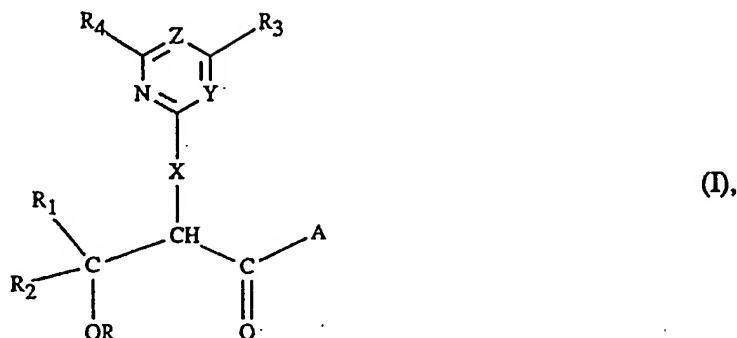
Table B2: Post-emergence action

| Test plants: Compound No. | Setaria | Sina- pis | Stel- laria | Sola- num | Ipo- moea |
|----------------------------------|---------|--------------|----------------|--------------|--------------|
| 1.001 (isomer I) | 1 | 1 | 2 | 1 | 2 |
| 1.002 (isomer II) | 2 | 1 | 1 | 1 | 3 |
| 1.065 (isomer I) | 3 | 1 | 2 | 2 | 3 |
| 1.065 (isomer II) | 2 | 1 | 2 | 2 | 1 |
| 1.066 (isomer I) | 3 | 1 | 3 | 2 | 2 |
| 1.088 + 1.089 (isomer I + II) | 6 | 2 | 3 | 2 | 2 |
| 1.088 (isomer I) | 6 | 1 | 2 | 2 | 2 |
| 1.089 (isomer II) | 5 | 1 | 2 | 2 | 2 |
| 2.001 (isomer I) | 2 | 1 | 2 | 1 | 3 |
| 2.002 (isomer II) | 1 | 1 | 1 | 1 | 2 |
| 3.051 (isomer I) | 3 | 1 | 2 | 1 | 2 |
| 4.002 (isomeric mixture) | 3 | 1 | 3 | 2 | 1 |
| 4.065 (isomer I) | 3 | 1 | 3 | 3 | 2 |
| 5.020 (isomeric mixture) | 1 | 1 | 2 | 1 | 2 |
| 5.048 (isomer II) | 3 | 1 | 3 | 2 | 2 |
| 7.002 (isomer I) | 2 | 1 | 2 | 1 | 2 |

The same results are obtained when the compounds of formula I are formulated in accordance with Examples F1, F2 and F4 to F8.

What is claimed is:

1. A compound of formula I



wherein

R is hydrogen, C₁-C₆alkyl, C₁-C₄haloalkyl, C₁- or C₂-alkyl substituted by C₁- or C₂-alkoxy, cyano, phenyl or phenyl substituted by halogen, methyl, methoxy or trifluoromethyl, C₃-C₆alkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl-C₁- or -C₂-alkyl, C₄-C₆cycloalkyl, C₁-C₄alkylcarbonyl or C₁-C₄alkylsulfonyl;

R₁ is C₁-C₇haloalkyl;

R₂ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₂-C₆alkenyl, C₃-C₆cycloalkyl, phenyl, phenyl substituted by fluorine, chlorine, bromine, trifluoromethyl or methoxy, 2-, 3- or 4-pyridyl, or 2- or 3-thienyl;

R₃ is methyl, ethyl, methoxy, ethoxy, trifluoromethyl, difluoromethoxy or 2,2,2-trifluoroethoxy;

Z is nitrogen, methine or methine substituted by fluorine, chlorine, bromine or methyl;

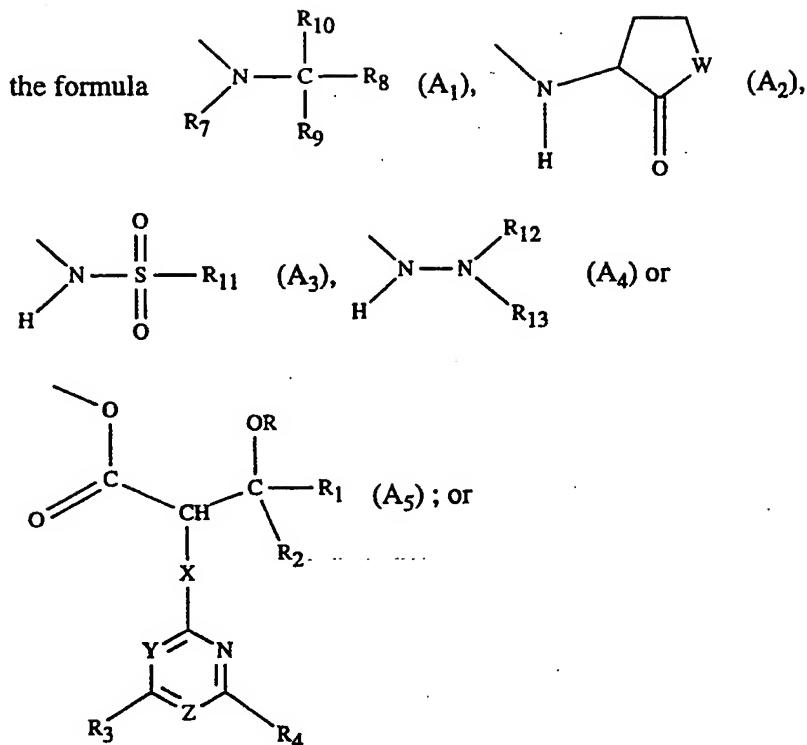
R₄ is fluorine, chlorine, methyl, ethyl, isopropyl, cyclopropyl, methoxy, ethoxy, methylthio, ethylthio, methylamino, dimethylamino, ethylamino, methoxymethyl, trifluoromethyl, chloromethyl, trichloromethyl or difluoromethoxy; or, if Z is methine, R₄ forms a -O(CH₂)_m bridge to Z, the linkage to Z being *via* the carbon atom;

Y is nitrogen, or, if Z is nitrogen, Y is nitrogen, methine or methine substituted by fluorine, chlorine or bromine;

X is oxygen or sulfur;

A is hydroxy, -OR₅, -SR₆, imidazolyl, triazolyl, 2-thionothiazolidin-3-yl, cyanamino, hydroxyamino, C₁-C₆alkoxyamino, C₁-C₃alkoxy(C₁-C₃alkyl)amino or a group of

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A and R together form a bond;

R₅ is C₁-C₆alkyl, C₃-C₆alkenyl, C₃-C₆alkynyl, C₁-C₄alkoxy-C₁-C₄alkyl, C₁- or C₂-alkoxy-ethoxy-C₁- or -C₂-alkyl, C₃- or C₄-alkenylloxy-C₁-C₄alkyl, C₃- or C₄-alkynyloxy-C₁-C₄alkyl, C₁-C₄alkylthio-C₁-C₄alkyl, C₁-C₄alkylsulfinyl-C₁-C₄alkyl, C₂-C₄dialkylamino-C₁-C₄alkyl, tri-C₁-C₆alkyl-silyl-C₁-C₄alkyl, C₁-C₄alkylcarbonyloxy-C₁- or -C₂-alkyl, C₁-C₄alkoxycarbonyl-C₁-C₆alkyl, C₃- or C₄-alkenyloxy carbonyl-C₁-C₆alkyl, C₃- or C₄-alkynyloxy carbonyl-C₁-C₆alkyl, C₁-C₄alkylthiocarbonyl-C₁-C₄alkyl, benzyloxycarbonyl-C₁-C₆alkyl, C₁-C₄alkoxy-carbonylmethyl-carbonylmethyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkyl-C₁-C₃alkyl, C₃-C₆oxacycloalkyl, C₃-C₆oxacycloalkyl substituted by C₁-C₃alkyl, C₂-C₆oxacycloalkyl-C₁-C₃alkyl, C₃-C₅dioxacycloalkyl, C₃-C₅dioxacycloalkyl substituted by C₁-C₃alkyl, C₃-C₅dioxacycloalkyl-C₁-C₃alkyl, benzyl, pyridylmethyl, C₁- or C₂-di-alkyl-phosphinyl, C₁-C₄alkylamino, dimethylamino, C₂-C₆alkylideneimino, (C₂-C₆alkylideneimino)-oxy-C₁- or -C₂-alkyl, phenyl, or phenyl substituted by fluorine, chlorine, bromine, methyl, methoxy or nitro;

R₆ is C₁-C₆alkyl, C₂-C₄dialkylamino-C₁-C₄alkyl, C₁-C₄alkoxycarbonyl-C₁-C₄alkyl, phenyl, or phenyl substituted by fluorine, chlorine, bromine, methyl, methoxy or nitro;

R₇ is hydrogen or methyl;

R₉ is hydrogen, trifluoromethyl, C₁-C₄alkyl, C₁-C₄alkyl substituted by hydroxy, C₁-C₄alkoxy, mercapto, C₁-C₄alkylmercapto, phenyl, 4-hydroxyphenyl, 4-imidazolyl, 3-indolyl, carboxy, C₁-C₄alkoxycarbonyl, C₃- or C₄-alkenyloxycarbonyl, cyano, carbamoyl, methylphosphino or methylsulfoximino, C₂-C₆alkenyl, C₂-C₆alkenyl substituted by chlorine, methyl or methoxy, ethynyl, cyclopropyl, phenyl or phenyl substituted by chlorine, methyl or methoxy; or

R₇ and R₉ together are -(CH₂)_q-, -CH₂CH(OH)CH₂-, -CH₂SCH₂- or -CH₂CH₂SCH₂-;

R₈ is hydroxymethyl, formyl, cyano, phosphono, phosphino, methylphosphino or a -COL group;

R₁₀ is hydrogen or methyl; or

R₉ and R₁₀ together are -(CH₂)_n-;

R₁₁ is C₁-C₆alkyl, C₁-C₆haloalkyl, C₂-C₆alkenyl, C₂-C₆haloalkenyl, C₂-C₆alkynyl, C₂-C₆haloalkynyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkylmethyl, C₁-C₄alkylamino, di-C₁-C₄alkylamino, C₁-C₃alkoxy-C₁-C₃alkylamino, C₃-C₆alkenylamino, C₃-C₆alkynylamino, C₃-C₆cycloalkylamino, morpholino, piperazino, piperidino, arylamino, arylamino substituted by fluorine, chlorine, methyl, trifluoromethyl, methoxy or benzylamino, pyridyl, pyridyl substituted by fluorine, chlorine, methyl, ethyl, methoxy, difluoromethoxy, trifluoromethyl, methylamino or C₁-C₃alkoxy-carbonyl, benzyl, phenyl or phenyl substituted by fluorine, chlorine, bromine, methyl, ethyl, trifluoromethyl, methoxy, difluoromethoxy, ethoxy, nitro, cyano or C₁-C₃alkoxycarbonyl;

R₁₂ is hydrogen or methyl;

R₁₃ is hydrogen, C₁-C₆alkyl, phenyl or phenyl substituted by fluorine, chlorine, bromine, iodine, C₁-C₄alkyl, trifluoromethyl, C₁-C₃alkoxy, difluoromethoxy, cyano, nitro or C₁-C₄alkoxycarbonyl, pyridyl or pyridyl mono- or di-substituted by fluorine, chlorine, methyl, methoxy or trifluoromethyl;

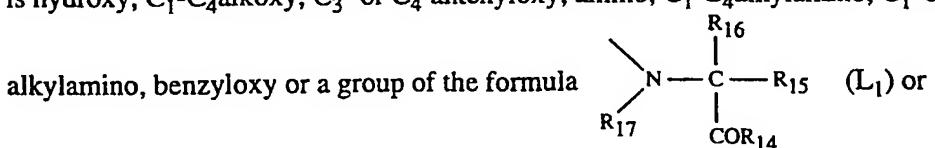
m is 2 or 3;

n is 2, 3, 4 or 5;

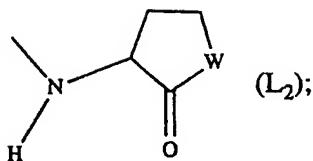
q is 2 or 3;

W is oxygen or sulfur;

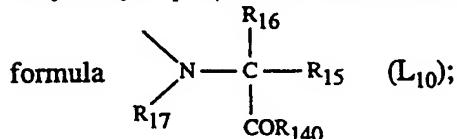
L is hydroxy, C₁-C₄alkoxy, C₃- or C₄-alkenyloxy, amino, C₁-C₄alkylamino, C₁-C₄di-alkylamino, benzyloxy or a group of the formula



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R₁₄ is hydroxy, C₁-C₄alkoxy, 2-propenyoxy, benzyloxy, amino or a further group of the



R₁₄₀ is hydroxy, C₁-C₄alkoxy, 2-propenyoxy, benzyloxy or amino;

R₁₅ is hydrogen, C₁-C₄alkyl or benzyl;

R₁₇ is hydrogen; or

R₁₅ and R₁₇ together are -(CH₂)₃-; and

R₁₆ is hydrogen or methyl;

or a salt of a compound of formula I that contains a carboxy or sulfonamide group, or a stereoisomer of a compound of formula I.

2. A compound according to claim 1, wherein R₂ is hydrogen, methyl, methyl substituted by fluorine, chlorine or bromine, ethyl, pentafluoroethyl, phenyl, phenyl mono- to penta-substituted by fluorine or mono- to di-substituted by chlorine, bromine, trifluoromethyl or methoxy, pyridyl or thienyl.

3. A compound according to claim 2, wherein R₂ is hydrogen, methyl, trifluoromethyl, chlorodifluoromethyl, dichlorofluoromethyl, dichloromethyl, trichloromethyl, dibromo-methyl, ethyl, pentafluoroethyl, phenyl, phenyl mono-substituted by fluorine, chlorine, tri-fluoromethyl or methoxy, 2- or 3-pyridyl or 2-thienyl.

4. A compound according to claim 3, wherein R₂ is methyl, trifluoromethyl, chloro-difluoromethyl, dichlorofluoromethyl, dichloromethyl or trichloromethyl.

5. A compound according to claim 1, wherein R₁ is C₁-C₃perhaloalkyl.

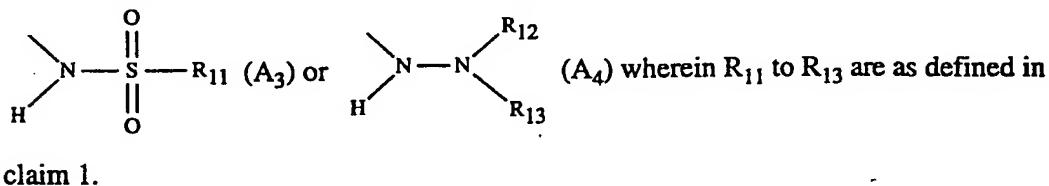
6. A compound according to claim 5, wherein R₁ is trifluoromethyl, chlorodifluoromethyl, dichlorofluoromethyl, trichloromethyl, tribromomethyl, pentafluoroethyl or heptafluoro-propyl.

7. A compound according to claim 6, wherein R₁ is trifluoromethyl.
8. A compound according to claim 1, wherein R₃ is methoxy; and R₄ is methyl, trifluoromethyl, chlorine, methoxy, difluoromethoxy, ethoxy or dimethylamino; or R₄ forms a -OCH₂CH₂- bridge to Z.
9. A compound according to claim 8, wherein R₃ and R₄ are methoxy.
10. A compound according to claim 1, wherein Z is methine.
11. A compound according to claim 1, wherein R₃ and R₄ are methoxy; and Z is methine.
12. A compound according to claim 1, wherein R is C₁-C₄alkyl, 2-propenyl, 2-propynyl, 2-fluoroethyl, 2-chloroethyl, 2-methoxyethyl, 2-cyanoethyl or benzyl.
13. A compound according to claim 12, wherein R is methyl or ethyl.
14. A compound according to claim 1, wherein R is hydrogen.
15. A compound according to claim 1, wherein A and R together form a bond.
16. A compound according to claim 1, wherein
 - A is hydroxy, C₁-C₄alkoxy, 2-propenyloxy, 2-propynyoxy, benzyloxy, C₁-C₄alkylcarbonyloxy-C₁- or -C₂-alkoxy, N,N-dimethylhydroxyamino, N-methoxyamino, cyanamino, or a group of the formula A₁, A₂, A₃ or A₄, wherein
 - R₈ is a -COL group and
 - L is as defined in claim 1;
 - R₇ is hydrogen;
 - R₉ is hydrogen or C₁-C₄alkyl; or
 - R₇ and R₉ together are -(CH₂)₃-;
 - R₁₀ is hydrogen;
 - R₁₁ is C₁-C₄alkyl, cyclopropyl, cyclopropylmethyl, C₃- or C₄-alkenyl, C₃- or C₄-haloalkenyl, cyclobutyl, trifluoromethyl, ethylamino, n-propylamino, 2-propynylamino, di-C₁-C₄alkylamino, N-methoxy-methylamino, morpholino, pyridyl or pyridyl substituted by halogen or by methoxycarbonyl, phenyl or phenyl mono- or disubstituted by fluorine, chlorine, bromine or methoxy; and

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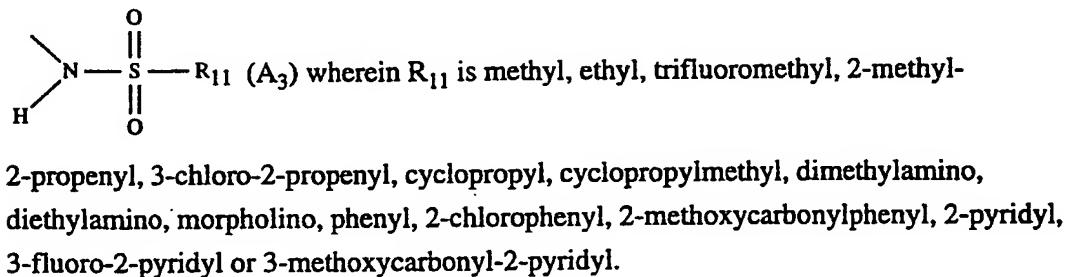
R_{13} is hydrogen, C_1 - C_4 alkyl, phenyl or phenyl mono- or di-substituted by fluorine, chlorine, methyl, trifluoromethyl, methoxy, methoxycarbonyl or nitro.

17. A compound according to claim 16, wherein A is hydroxy or a group of the formula

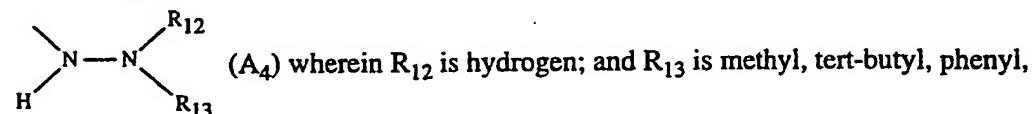


18. A compound according to claim 17, wherein A is hydroxy.

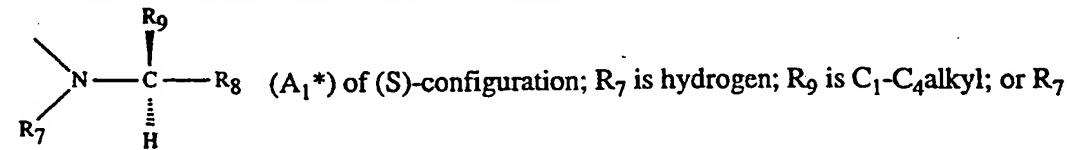
19. A compound according to claim 16, wherein A is a group of the formula



20. A compound according to claim 16, wherein A is a group of the formula

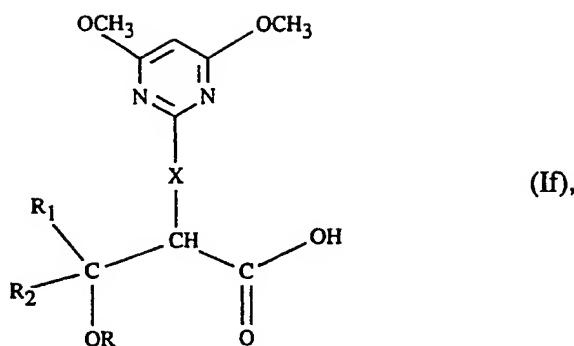


21. A compound according to claim 16, wherein A is a group of the formula



22. A compound according to claim 1 of formula If

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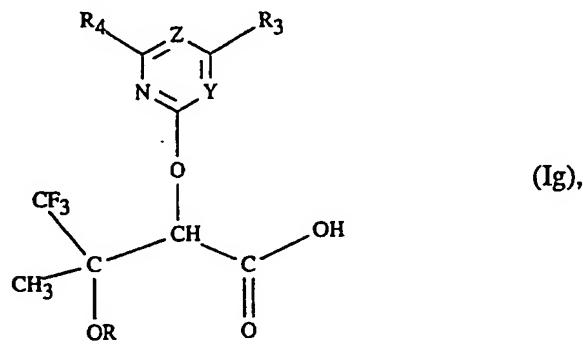
wherein

R is hydrogen, methyl, ethyl, difluoromethyl, 2-fluoroethyl, 2-chloroethyl, 2-cyanoethyl, 2-methoxyethyl, 2-ethoxyethyl, n-propyl, 2-propenyl, 2-propynyl or benzyl;

R₁ is trifluoromethyl, chlorodifluoromethyl, trichloromethyl, tribromomethyl, pentafluoroethyl or heptafluoropropyl; and

R₂ is hydrogen, methyl, trifluoromethyl, chlorodifluoromethyl, dichlorofluoromethyl, dichloromethyl, trichloromethyl, dibromomethyl, ethyl, pentafluoroethyl, phenyl, phenyl mono-substituted by fluorine, chlorine, trifluoromethyl or methoxy, 2- or 3-pyridyl or 2-thienyl.

23. A compound according to claim 1 of formula Ig



wherein

R is methyl, ethyl, difluoromethyl, 2-fluoroethyl, 2-chloroethyl, 2-cyanoethyl, 2-methoxyethyl, 2-ethoxyethyl, n-propyl, 2-propenyl, 2-propynyl or benzyl;

R₃ is methoxy or ethoxy;

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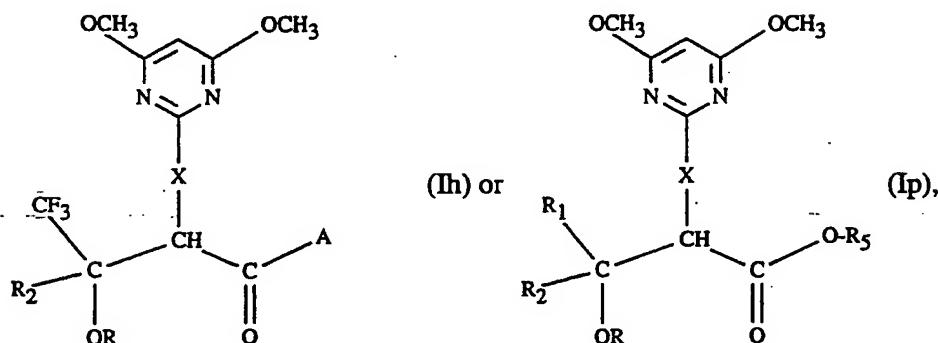
R₄ is methyl, trifluoromethyl, trichloromethyl, methoxy, difluoromethoxy, methylamino, dimethylamino, methylthio or cyclopropyl;

Y is nitrogen, methine or chloromethine; and

Z is nitrogen or methine; or

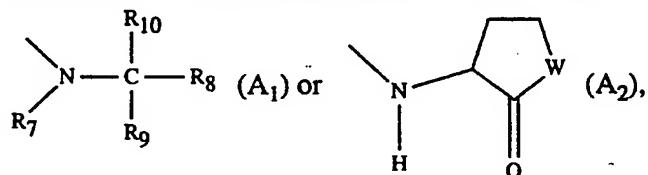
R₄ forms a -O(CH₂)₂- bridge to Z.

24. A compound according to claim 1 of formula I_h or I_p



wherein

R is hydrogen, methyl, ethyl, difluoromethyl, 2-fluoroethyl, 2-chloroethyl, 2-cyanoethyl, 2-methoxyethyl, 2-ethoxyethyl, n-propyl, 2-propenyl, 2-propynyl or benzyl;
 R₂ is methyl, phenyl or trifluoromethyl;
 A is methoxy, ethoxy, tert-butoxy, 2-propenoxy, 2-propylideneiminoethoxy, N,N-dimethylaminoxy, cyanamino, methoxyamino, imidazolyl or a group of the formula



wherein

R₇ is hydrogen;

R₉ is hydrogen, C₁-C₄alkyl or C₁-C₄alkyl substituted by carboxy, phenyl, methylphosphino or methylthio; or

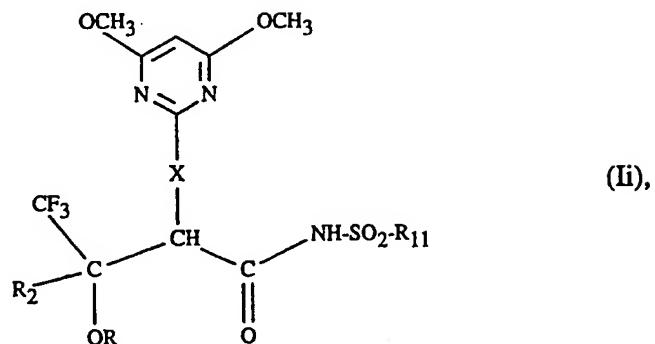
R₇ and R₉ together are -(CH₂)₃-;

R₈ is methylphosphino or a -COL group, and L is hydroxy or C₁-C₄alkoxy; and

R₁₀ is hydrogen.

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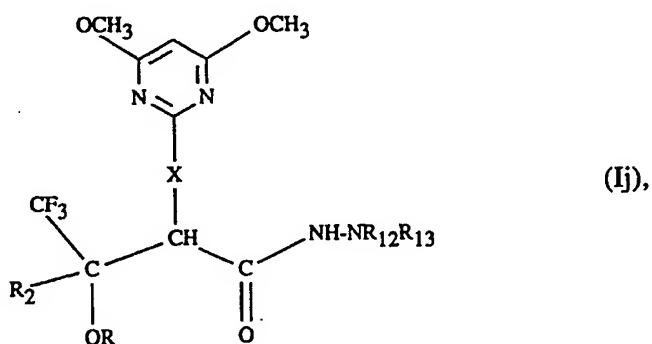
25. A compound according to claim 1 of formula II



wherein

R is hydrogen, methyl, ethyl, difluoromethyl, 2-fluoroethyl, 2-chloroethyl, 2-cyanoethyl, 2-methoxyethyl, 2-ethoxyethyl, n-propyl, 2-propenyl, 2-propynyl or benzyl;
 R₂ is methyl or trifluoromethyl; and
 R₁₁ is methyl, ethyl, trifluoromethyl, 2-methyl-2-propenyl, 3-chloro-2-propenyl, cyclopropyl, dimethylamino, diethylamino, morpholino, phenyl, 2-chlorophenyl, 2-methoxycarbonylphenyl, 2-pyridyl, 2-fluoro-3-pyridyl or 3-fluoro-2-pyridyl.

26. A compound according to claim 1 of formula Ij



wherein

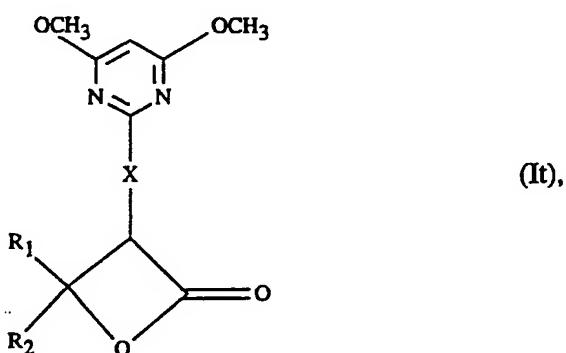
R is hydrogen, methyl, ethyl, difluoromethyl, 2-fluoroethyl, 2-chloroethyl, 2-cyanoethyl, 2-methoxyethyl, 2-ethoxyethyl, n-propyl, 2-propenyl, 2-propynyl or benzyl;
 R₂ is methyl, trifluoromethyl or phenyl;

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R_{12} is hydrogen or methyl; and

R_{13} is methyl, tert-butyl, phenyl, 2-chlorophenyl, 2-fluorophenyl, 2-tolyl, 2,4-difluorophenyl, 4-chlorophenyl, 3-trifluoromethylphenyl or 4-methoxyphenyl.

27. A compound according to claim 1 of formula Ia



wherein

X is oxygen or sulfur;

R_1 is trifluoromethyl, pentafluoroethyl or heptafluoropropyl; and

R_2 is methyl, ethyl, trifluoromethyl or phenyl.

28. A compound in the form of a mixture of stereoisomers or in the form of the pure isomer according to claim 1, selected from:

2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3-trifluoromethylbutyric acid;

2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-hydroxy-3-trifluoromethylbutyric acid;

2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-ethoxy-3-trifluoromethylbutyric acid;

2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methyl-3-trifluoromethyl-oxetanone;

2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-methoxy-3-trifluoromethylbutyric acid;

2-[(4,6-dimethoxy-pyrimidin-2-yl)-oxy]-3-ethoxy-3-trifluoromethylbutyric acid;

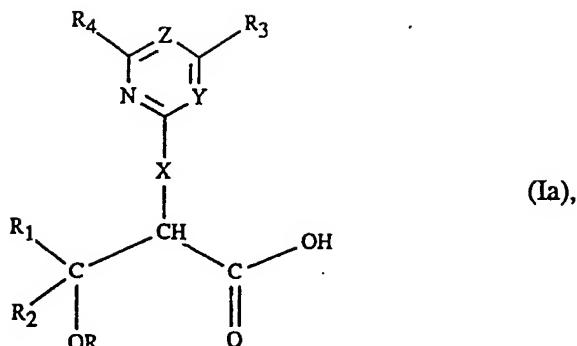
2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-methoxy-3,3-bis-trifluoromethylpropionic acid;

and

2-[(4,6-dimethoxy-pyrimidin-2-yl)-thio]-3-hydroxy-3,3-bis-trifluoromethylpropionic acid.

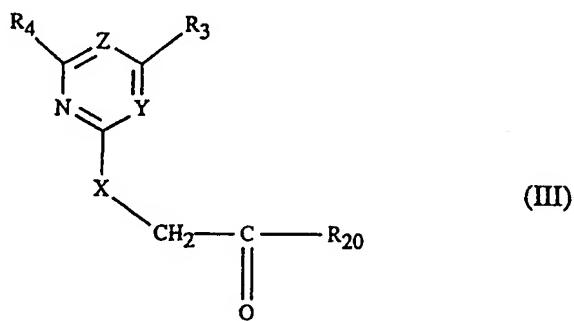
29. A process for the preparation of a compound of formula Ia

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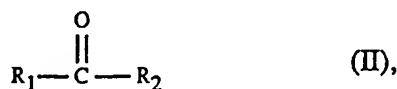


wherein R₁ to R₄, X, Y and Z are as defined in claim 1 and R is C₁-C₆alkyl, C₁-C₄halo-alkyl, C₁- or C₂-alkyl substituted by C₁- or C₂-alkoxy, cyano, phenyl or phenyl substituted by halogen, methyl, methoxy or trifluoromethyl, C₃-C₆alkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl-C₁- or -C₂-alkyl, C₄-C₆cycloalkyl, C₁-C₄alkylcarbonyl or C₁-C₄alkylsulfonyl, according to claim 1, which process comprises

reacting a compound of formula III

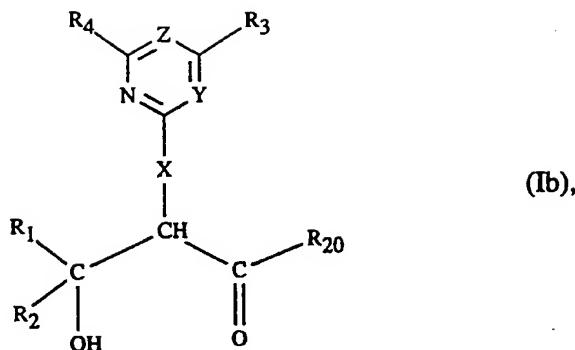


with a compound of formula II



in the presence of a suitable base, to form a compound of formula Ib

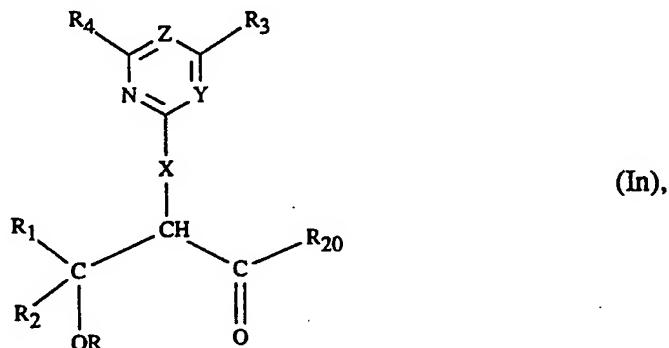
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wherein in the compounds of formulae III, II and Ib the radicals R₁ to R₄, X, Y and Z are as defined in claim 1 and R₂₀ is C₁-C₆alkoxy, chloroethoxy, 2-trimethylsilylethoxy, 2-propenyloxy, benzyloxy or benzyloxy substituted by methoxy, and then alkylating, acylating or sulfonylating the compound of formula Ib with a compound of formula IX



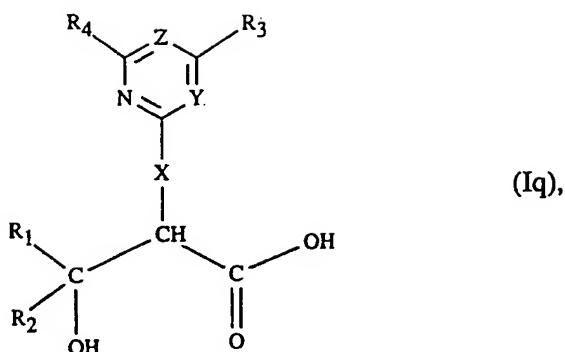
wherein R is as defined and L₅ is a leaving group, where appropriate in the presence of a base and a suitable solvent, to form the compound of formula In



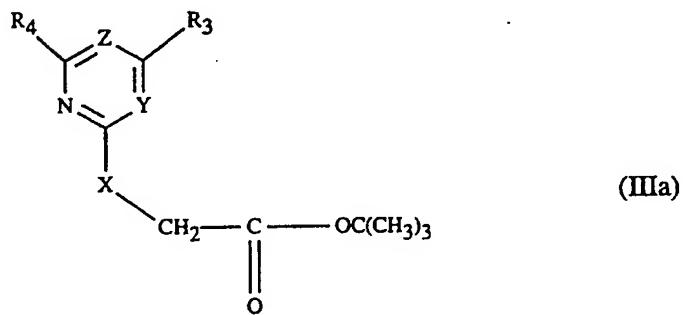
and then reacting that compound of formula In further under hydrolytic or hydrogenolytic conditions or, when R₂₀ is the tert-C₄H₉-O- group, under acid-catalysed conditions.

30. A process for the preparation of a compound of formula Iq

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wherein R₂ to R₄, X, Y and Z are as defined in claim 1 and R₁ is C₁-C₇alkyl or C₁-C₇halo-alkyl, or R₁ together with R₂ is -(CH₂)₄- or -(CH₂)₅-, according to claim 1, which process comprises reacting a compound of formula IIIa

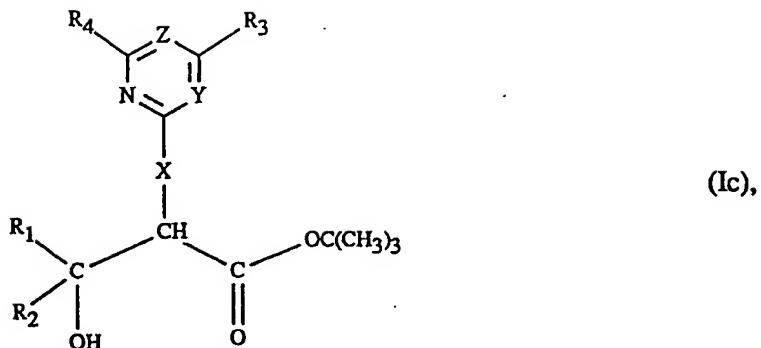


with a compound of formula II



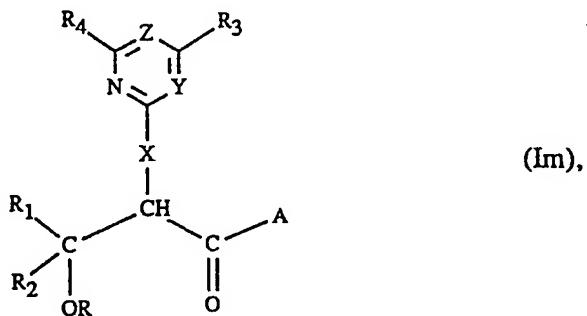
in the presence of a suitable base, to form a compound of formula Ic

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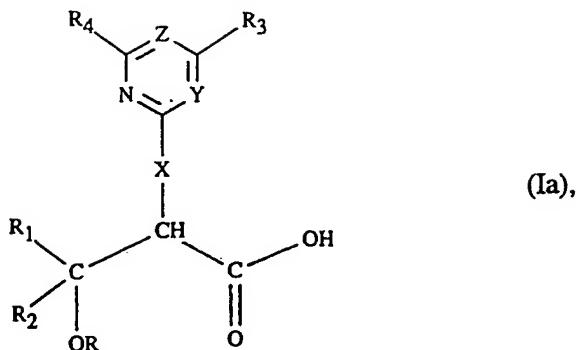
wherein in the compounds of formulae IIIa, II and Ic the radicals R₂ to R₄, X, Y and Z are as defined and R₁ is C₁-C₇alkyl or C₁-C₇haloalkyl, or R₁ together with R₂ is -(CH₂)₄- or -(CH₂)₅-, and then hydrolysing the compound of formula Ic with trifluoroacetic acid, sulfuric acid, phosphoric acid or a mixture of sulfuric acid and acetic acid, where appropriate in the presence of an additional solvent.

31. A process for the preparation of a compound of formula I_m



wherein R₁ to R₄, X, Y and Z are as defined in claim 1, R is C₁-C₆alkyl, C₁-C₄haloalkyl, C₁- or C₂-alkyl substituted by C₁- or C₂-alkoxy, cyano, phenyl or phenyl substituted by halogen, methyl, methoxy or trifluoromethyl, C₃-C₆alkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl-C₁- or -C₂-alkyl, C₄-C₆cycloalkyl, C₁-C₄alkylcarbonyl or C₁-C₄alkylsulfonyl and A is -OR₅, -SR₆, cyanamino or a group A₁ to A₄, according to claim 1, which process comprises converting a compound of formula Ia

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wherein R, R₁ to R₄, X, Y and Z are as defined,

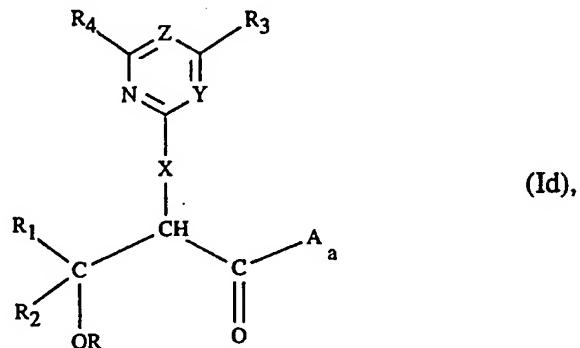
a) by reaction with a compound of formula VII



wherein

A_a is a leaving group, especially chlorine, bromine, 2,4,6-triisopropylphenyl-sulfonyl, imidazolyl, triazolyl, 2-thionothiazolidin-3-yl or N,N'-dicyclohexyl-isoureidyl, and

L_3 is -S(O)Cl, -C(O)Cl, -C(O)-C(O)Cl, -PCl₄, -P(O)Cl₂, -P(O)Br₂, 2,4,6-triisopropyl-phenyl-sulfonyl, imidazolyl, triazolyl, N-carbonylimidazole or N-carbonyltriazole, into the compound of formula Id



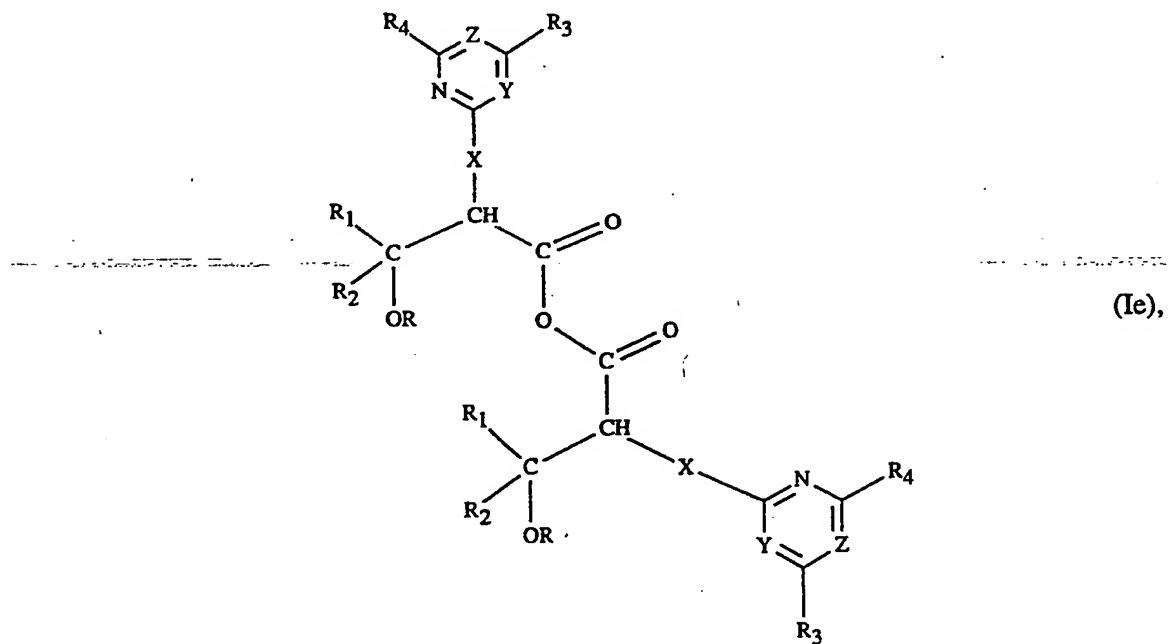
wherein R₁ to R₄, X, Y and Z are as defined in claim 1 and R and A_a are as defined above, and then reacting the compound of formula Id with a compound of formula V



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wherein A is -OR₅, -SR₆, cyanamino or a group A₁ to A₄, where appropriate in the presence of a base and a solvent; or

b) by treatment with a water-removing reagent, such as phosphorus oxychloride, into the compound of formula Ie



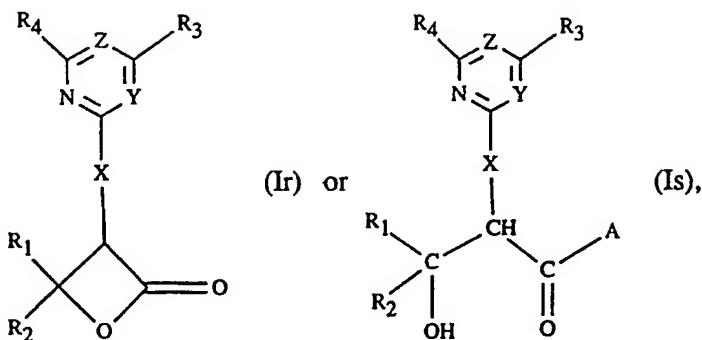
wherein R₁ to R₄, X, Y and Z are as defined in claim 1 and R is as defined above, and then reacting the compound of formula Ie with a compound of formula V

A-H (V),

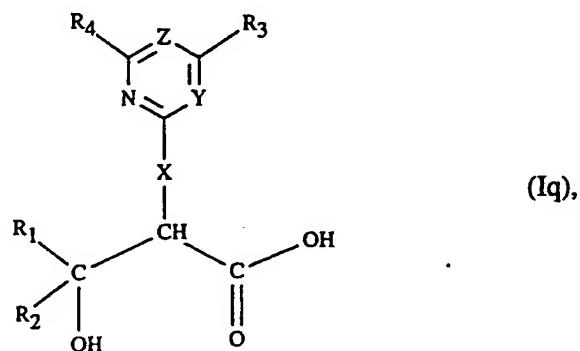
wherein A is -OR₅, -SR₆, cyanamino, hydroxyamino, C₁-C₆alkoxyamino, C₁-C₃alkoxy-(C₁-C₃alkyl)amino or a group A₁ to A₄, where appropriate in the presence of a base and a solvent.

32. A process for the preparation of a compound of formula Ii or Ii

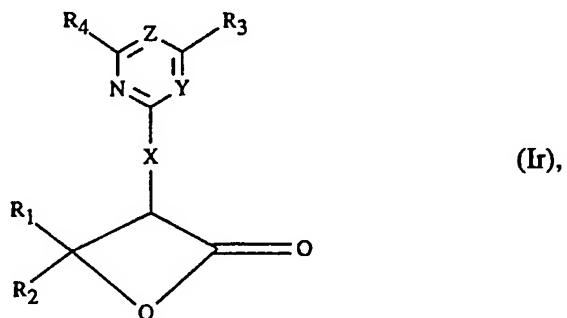
- 108 -



wherein R_2 to R_4 , X, Y, Z and A are as defined in claim 1 and R_1 is C_1 - C_7 alkyl or C_1 - C_7 haloalkyl, or R_1 together with R_2 is $-(CH_2)_4-$ or $-(CH_2)_5-$, according to claim 1, which process comprises converting a compound of formula Iq



wherein R_1 to R_4 , X, Y and Z are as defined, by treatment with a water-removing reagent, such as phosphorus oxychloride, into the compound of formula Ir



wherein R_2 to R_4 , X, Y and Z are as defined in claim 1 and R_1 is C_1 - C_7 alkyl or C_1 - C_7 haloalkyl, or R_1 together with R_2 is $-(CH_2)_4-$ or $-(CH_2)_5-$, and then reacting the compound of

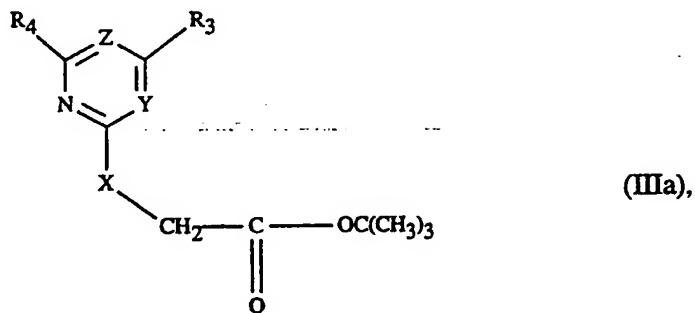
- 109 -

formula I_r with a compound of formula V

A-H (V),

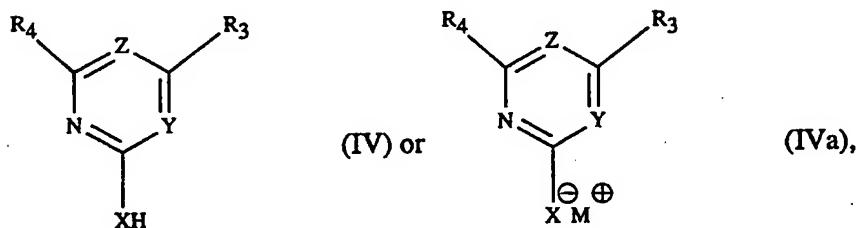
wherein A is hydroxy, -OR₅, -SR₆, cyanamino, hydroxyamino, C₁-C₆alkoxyamino, C₁-C₃alkoxy-C₁-C₆alkylamino or a group A₁ to A₄, where appropriate in the presence of a base and a solvent.

33. A process for the preparation of a compound of formula IIIa



wherein R₃, R₄, X, Y and Z are as defined in claim 1, which process comprises

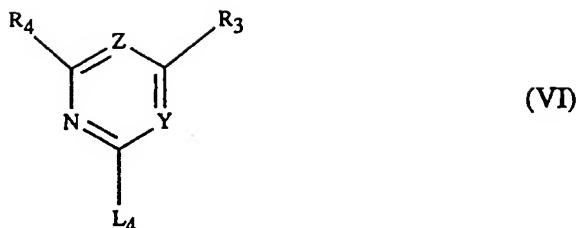
a) reacting a compound of formula IV or IVa



wherein M[⊕] is a cation, with bromo- or chloro-acetic acid tert-butyl ester in the presence of a base and a suitable solvent; or

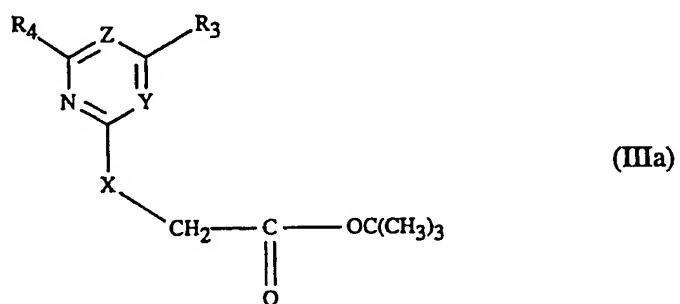
b) reacting a compound of formula VI

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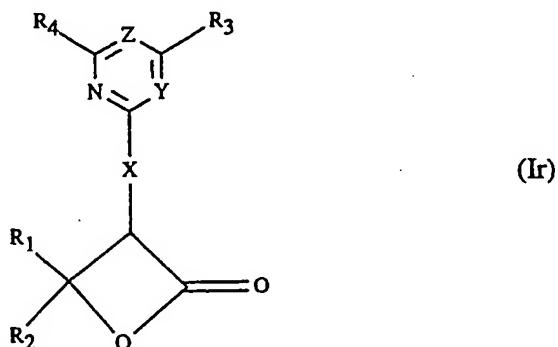
with hydroxy- or mercapto-acetic acid tert-butyl ester (VIII) in the presence of a base and a suitable solvent; in the compounds of formulae IV and VI the radicals R₃, R₄, X, Y and Z are as defined in claim 1 and L₄ is a leaving group, preferably fluorine, chlorine, methylsulfonyl or benzylsulfonyl.

34. A compound of formula IIIa



wherein R₃, R₄, Z, Y and X are as defined in claim 1.

35. A compound of formula I_r



wherein R₂ to R₄, X, Y and Z are as defined in claim 1 and R₁ is C₁-C₇alkyl, or R₁

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together with R₂ is -(CH₂)₄- or -(CH₂)₅-.

36. A herbicidal and plant-growth-inhibiting composition, which comprises one or more compounds of formula I, according to claim 1.

37. A composition according to claim 36, which comprises from 0.1 % to 95 % of compound of formula I according to claim 1.

38. A method of controlling undesired plant growth, which comprises applying an effective amount of a compound of formula I, according to claim 1, or of a composition comprising that compound, to the plants or to the locus thereof.

39. A method according to claim 38, which comprises applying a compound of formula I in an amount of from 0.001 to 2 kg per hectare.

40. A method of inhibiting plant growth, which comprises applying an effective amount of a compound of formula I, according to claim 1, or of a composition comprising that compound, to the plants or to the locus thereof.

41. A method according to claim 38 for the selective pre- or post-emergence control of weeds in crops of useful plants, especially cereals, maize, rice, soybeans, rape and cotton.

42. The use of a composition according to claim 36 in the selective pre- or post-emergence control of weeds in crops of useful plants, especially cereals, maize, rice, soybeans, rape and cotton.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 95/02295A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D239/60 A01N43/40 C07D405/12 C07D401/00 C07D233/54
C07D401/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| A | EP,A,0 481 512 (UBE INDUSTRIES,LTD.) 22 April 1992 cited in the application see claims --- | 1,36 |
| A | EP,A,0 567 014 (UBE INDUSTRIES,LTD.) 27 October 1993 cited in the application see claims --- | 1,36 |

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Date of the actual completion of the international search

29 August 1995

Date of mailing of the international search report

- 5. 09. 95

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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| A | EP,A,0 347 811 (KUMAI CHEMICAL INDUSTRY CO.) 27 December 1989 cited in the application * page 29, table 2 * --- | 1,36 |
| A | WO,A,93 25540 (CIBA-GEIGY AG) 23 December 1993 cited in the application * claims, r3= ... haloalkyl, ... * --- | 1,36 |
| P,A | WO,A,94 25442 (BASF AG) 10 November 1994 * claims, R5 = ... haloalkyl, ...* ----- | 1,36 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern: Application No

PCT/EP 95/02295

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
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